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Modeling study on the neopentyl+ O2 reaction system and experimental and modeling study on MTBE pyrolysis and oxidation

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MODELING STUDY ON THE NEOPENTYL + O_2 REACTION SYSTEM AND EXPERIMENTAL AND MODELING STUDY ON MTBE PYROLYSIS AND OXIDATION

by
Ru Wei

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MODELING STUDY ON THE NEOPENTYL + O_2 REACTION SYSTEM AND EXPERIMENTAL AND MODELING STUDY ON MTBE PYROLYSIS AND OXIDATION

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ABSTRACT

MODELING STUDY ON THE NEOPENTYL + O_2 REACTION SYSTEM AND EXPERIMENTAL AND MODELING STUDY ON MTBE PYROLYSIS AND OXIDATION

by
Ru Wei

A modeling study on neopentyl radical + O_2 reaction system is conducted in this study. Thermodynamic parameters on all species and important transition states are calculated. A thermochemical kinetic analysis is performed.

Thermodynamic parameters are estimated using group additivity with HBI groups. Transition state energies are evaluated from experimental and theoretical data in the literature, combined with elementary reaction modeling to account for temperature effects. Transition state structures, vibration frequencies and entropies are determined from semi-empirical calculations, MOPAC PM3. Kinetics are analyzed with quantum RRK theory for k(E) coupled with modified strong collision analysis of Gilbert et al for fall-off. An elementary reaction mechanism is constructed to model experimental data in the literature focusing on this neopentyl + O_2 reaction system.

Experimental and modeling studies are conducted for methyl *tert*-butyl ether (MTBE) pyrolysis and oxidation. Experimental data are presented in argon diluent in a high pressure, flow reactor over a wide temperature range and at three pressures of 4, 7, 10 atm. Three equivalence ratios were selected for the study of oxidation of MTBE. On-

line GC-FID was used to analyze reacted mixture from flow reactor. Iso-butene and methanol are observed as major products from both oxidation and pyrolysis of MTBE experiments. Acetone, formaldehyde, propene and methane are additional important products.

A detailed, pressure and temperature dependent, kinetic model is developed for the pyrolysis and oxidation of MTBE. The mechanism includes oxidation and thermal decomposition of the major products and other important intermediates. Thermodynamic parameters, transition states and kinetics are estimated, evaluated and analyzed as in the neopentyl modeling work.

Chebyshev polynomials (7×3) incorporate the pressure and temperature dependence into rate constant expressions. A modified Chemkin Interpreter is used to incorporate the combined pressure and temperature dependent rate expressions into the Chemkin integrators.

A specific reaction series: one of β-scission of C.CR'COOH, hydroperoxy alkyl radical to form an olefin plus a hydroperoxy methyl radical RC.OOH. This RC.OOH rapidly decompose to lower energy products: RCHO + OH. Little or no evidence is observed for formation of the final products in the transition state of the first β-scission step.

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This dissertation is dedicated to
my beloved family

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PART I

THERMO CHEMICAL AND THERMO CHEMICAL KINETIC MODELING

CHAPTER 1

RADICAL AND MOLECULE THERMO CHEMICAL KINETICS

1.1 Overview

Thermodynamic properties of molecules and radicals are important in many fields of science and research. Several important applications of these thermodynamic properties include: calculation of energy balance; equilibrium considerations; stability; reaction path analysis; spontaneity of reaction; kinetics versus thermodynamic control; theoretical reaction yields and detailed chemical reaction mechanism integration (reverse rate calculation).

An important era in chemical engineering optimization calculations and reactor design techniques is rapidly developing. It entails incorporation and use of detailed reaction kinetic mechanisms, which are based on fundamental thermodynamic and kinetic principles into a comprehensive computer code to model an entire reaction system and reactor using: (1) detailed mass balance from elemental composition; (2) energy conservation based on specific heat capacities and reactor heat flow; (3) thermodynamic properties of each species (atoms, molecules and radicals) incorporated into the mechanism for assurance of correct equilibrium determination; and (4) numerical integration of stiff Ordinary Differential Equations (ODE) describing the reaction for appropriate time, pressure and temperature profile(s), yielding complete product distribution and reagent conversion information. The code will also calculate sensitivity to input reagent concentrations and specific reactions in the mechanism, at different reaction time, should one wish to further optimize a mechanism using new experiment data.

Thermodynamic data on stable species, radicals and reaction transition states is critical in determining energy balance in chemical reactions and in calculation of the Gibbs Free Energy of a reaction and thus the equilibrium constant as a function of temperature, as well as to kinetic paths.

The use of detailed reaction kinetic mechanisms, based on fundamental principles in chemical kinetic theory, e.g. Transition State Theory, and on thermodynamic properties of the reacting species ($\Delta H_f(T)$, $\Delta S(T)$, and $C_p(T)$), allows the code (integration of reaction mechanism) to accurately predict results into regimes well outside those in the calibration experiments under which the mechanism was developed. Further more those codes can be reduced to reasonable numbers of detailed reaction steps by use of available computer sensitivity analysis codes for elimination of non-important reactions. This yields strong insight into the important elementary reaction steps and allows the optimizer code to function in a reasonable computer time requirement. To implement these computer codes, one has to have developed an accurate reaction mechanism and the thermodynamic database. The first step in derivation of the kinetic mechanism is development of the thermo database, which stress the key position of thermo database in the computer modeling work for related fields.

The way used to obtain thermodynamic properties for involved species in the current study is Group Additivity (THERM) and MOPAC calculation. Group database was developed by the Bozzelli group in NJIT. Enthalpies of formation of groups were obtained by evaluation of literature data. Entropies and heat capacities for stable species were calculated using the Rigid Rotor Harmonic Oscillator approximation taking into account the contributions from translation, rotations, vibrations and internal rotations.

Proper account was also taken of symmetry and optical isomers. Moments of inertia and fundamental frequencies were obtained using semi-empirical MNDO/PM3 calculations in the MOPAC 6.0 package. Barriers for internal rotations were adopted from appropriate experimental data or ab initio studies. Pitzer and Gwinn's approach was used to calculate the contributions of hindered rotors.

1.2 Group Additivities (THERM)

The Group Additivity methods was initially developed by Benson and Buss [1], from which one can often determine easier and faster than if one needed to search through the literature. This exists as a basis data set of reasonable and easily accessible size, from which one can determine thermodynamic parameters for a very large number of organic molecules and radicals.

The computer program THERM [2] performs group additivity calculations. The basic principle of calculations for molecules and radicals are illustrated as following.

1.2.1 Molecules

In the Group Additivity method, molecules are broken up into groups on the central atoms. The central atoms are those with more than one bond. Each C, O, N, S in a molecule is a group atom while H, Cl and F are not central atoms or group atoms. Each group is further identified by the specific species that are bonded to it. For example, the neopentane molecule, $(CH_3)_4C$ can be divided into 5 groups, they are: one group "C/C4", which means 4 carbon atoms bonded to central carbon atom which is located in the first

position of the group ID, and four identical groups "C/C/H3", which means one carbon atom and three hydrogen atoms bonded to central carbon atom.

Thermodynamic properties of a molecule can then be attributed to the sum of the properties of all groups within the molecule. The entropy obtained from group additivity is an Intrinsic Entropy, which does not consider the symmetry of the molecules. To get the actual entropy (Extrinsic Entropy) of stable molecules one needs to correct for symmetry. This is done by subtracting a term - $R\ln\sigma$ (R is 1.987 cal-mol^{-1}, ln is natural log and σ is the symmetry of the molecule), from the intrinsic entropy (Si) which results from adding the group values, that is $S = Si - R\ln\sigma$. Enthalpies and heat capacities are obtained directly from Group Additivity.

1.2.2 Radicals

Radical species are extremely important intermediates and reaction initiators in gas phase chemical systems. Accurate knowledge of their thermodynamic properties permits estimation of kinetic activation energies, calculation of important equilibrium values and, from the principles of microscopic reversibility, calculation of reverse reaction rates. All of these parameters are requirements for the kinetic modeling study.

1.2.2.1 Methods

Thermodynamic properties of radicals can be obtained in two ways. One of the methods, similar to molecules, is addition of values from all groups plus symmetry correct for entropies. This method needs one special group with a radical site on one central atom,

and it is difficult to find or assign thermodynamic parameters for such groups based on literature and experimental results.

The method used to calculate almost all radical species involved in current studies (Part II and Part III) is based on the Hydrogen atom Bond Increment (HBI) technique developed in this research group [3-4]. The HBI group technique is based on known thermodynamic properties of the parent molecule and the calculated changes that occur upon formation of a radical via loss of a H atom. The HBI group incorporates evaluated carbon hydrogen (C—H) or oxygen hydrogen (O--H) bond energies, for $\Delta H_f(298)$ of the respective radical, and entropy and heat capacity changes that result from loss or changes in vibration frequencies, internal rotation, and spin degeneracy when a hydrogen atom is removed from the specific carbon site.

Enthalpies of radicals are calculated by considering the following homologous reaction:

$$RH \Rightarrow R. + H., \qquad \Delta H^\circ_{rxn,298} = D(R\text{--}H) \text{ Bond Energy}$$

Then, the radical enthalpies of formation can be written as:

$$\Delta H^\circ_{rxn,298}(R.) = D(R\text{--}H) + \Delta H^\circ_{rxn,298}(RH) - 52.1 \text{ kcal-mol}^{-1}$$

One can calculate $\Delta H^\circ_{rxn,298}(R.)$ if one knows the bond strength for the R--H bond being broken to form the radical and H atom, and $\Delta H^\circ_{rxn,298}(RH)$.

Entropy and heat capacity can also be estimated, to a reasonable degree from those of the parent molecule. The molecular structure of a radical (R.) can be considered, to some extent, to be similar to that of the corresponding stable molecule (RH). The unpaired electron on the radical-centered atom is replaced by a bond to a H atom in the stable molecule while most of molecule sequence and chemical bonds basically remain the same

in the two species. If the differences in molecular structure and properties for R. and RH are properly taken into account, one can calculate $S°_{298}$ and $C_p(T)$ values for R. from properties of the corresponding RH parent plus increment values for $\Delta C_p(T)$ and $\Delta S°_{298}$ that account for these changes:

$S°_{int,298}$ (R.) = $S°_{int,298}$ (RH) + $\Delta S°_{298}$

$C_p(T)$ (R.) = $C_p(T)$ (RH) + $\Delta C_p(T)$

where $S°_{int}$ represents the intrinsic entropy (excluding symmetry).

These $\Delta S°_{298}$ and $\Delta C_p(T)$ ($300 \leq T/K \leq 1500$) increments are group (HBI) values for estimating entropy and heat capacity for radical from the parent. The real entropy for radical species should consider symmetry correction. So if one calculates entropy and heat capacity for a radical based on the parent molecule, one should incorporates the followings:

(1) Entropy and heat capacity increments accounting for loss and for the differences in vibration frequencies of a parent molecule losing a H atom to form the radical.

(2) Gain of inversion frequencies at radical centers of carbon atoms.

(3) Entropy and heat capacity corrections accounting for the differences of rotational barriers of internal rotors in parent and radical.

(4) Entropy corrections for electron spin degeneracy

(5) Entropy corrections for changes in symmetry between parent and radical (this is not included in the HBI groups but is done in THERM)

(6) Changes of mass (about accounting for 0.1 cal-mol^{-1})

The calculation of entropy and heat capacity for a radical are:

$$S°_{298}(R.) = S°_{298}(RH) + \Delta S°_{298}(HBI) + R\ln(\sigma_{radical}/\sigma_{parent})$$

where $\sigma_{radical}$ and σ_{parent} are the symmetry number for radical and the corresponding parent molecule. No further correction is required for the calculation of heat capacity using the HBI term value:

$$C_p(T)(R.) = C_p(T)(RH) + \Delta C_p(T)$$

1.2.2.2 Example of HBI Group Application

As an example, we consider formation of C_2H_5 from C_2H_6.

Loss of H atom results in the loss of one C-H stretch, two H-C-H bends and one H-C-C bend, and gain of one inversion motion of radical center because the normal rigid tetrahedral structure has been replaced with a more flexible, non-planar configuration. This loss of four frequencies and gain of one are used to account for the vibration frequency differences for HBI group, via the equation: $S/R = -\ln(1-e^{-x}) + x/(e^x - 1)$, $x = hc\nu/kT$, ν is frequencies and other have common meanings, between the ethyl radical and ethane parent, and get a value of 0.336 cal-mol^{-1}.

The difference in rotation barriers, 2.9 kcal-mol^{-1} and 0.1 kcal-mol^{-1}, for ethane and ethyl radical respectively, accounts for a significant fraction of $\Delta S°_{298}$ and $\Delta C_p(T)$ contribution to HBI values via "Pitzer and Gwinn Tables"[5 - 8], and results in a value of 0.892 cal-mol^{-1} for $\Delta S°_{298,int\text{-}rot.}$

Because all free radicals estimated in HBI techniques are considered to have only one unpaired electron (doublet) and assumed spin degeneracy equal to 2. Term Rln2 (1.38 cal-mol^{-1}) is already included into the HBI group.

The other very important correction for entropy is symmetry, which is not included in the HBI group but is done with computer code THERM. In ethyl radical and ethane molecule case, $\sigma_{radical}$ is 6 and σ_{parent} is 18, the $R\ln(\sigma_{radical}/\sigma_{parent})$ turn out value of 2.18 cal-mol^{-1}.

So, the entropy of ethyl radical is:

$$S°_{298}(C_2H_5\cdot) = S°_{298}(C_2H_6) + \Delta S°_{298}(HBI) + R\ln(\sigma_{radical}/\sigma_{parent})$$

$$= S°_{298}(C_2H_6) + (0.336 + 0.892 + 1.38) + 2.18 + 0.1$$

$$= S°_{298}(C_2H_6) + 4.888 \text{ (cal-mol}^{-1}\text{-K}^{-1}\text{)}$$

1.3 MOPAC

MOPAC is a general-purpose semi-empirical molecular orbital package for the study of chemical structures and reactions. MOPAC [9-10] calculates the vibration spectra, thermodynamic quantities, isotopic substitution effects and force constants for molecules, radicals, ions, and polymers. MOPAC is also available for locating a transition-state for the chemical reactions. As a relatively higher level calculation method in this study, MOPAC has been used for obtaining thermodynamic properties for molecules, radicals and transition states when it becomes necessary to find transition states for some important reactions, such as isomerization reaction, beta scission reactions and cyclic product formation reactions, involved in this modeling studies. MOPAC is also used as a more accurate and precise calculation tool to calculate thermodynamic properties for some species when THERM is not available or is not accurate enough.

Entropies, heat capacities and frequencies are calculated by using semi-empirical (MOPAC PM3) calculations modified by separately including the contributions from internal rotors, spin degeneracy (for radicals and transition states) and correction for optical isomers. The semi-empirical (MOPAC PM3) calculations can also be used to define transition state structures and obtain Arrhenius A factors for reactions including Isomerization, Elimination (Beta scission), Addition and Epoxide + OH (oxetan formation). These data are coupled into the QRRK fall-off calculations to determine the A factors as a function of temperature.

1.3.1 Molecules

The first step to calculate thermodynamic properties for molecules is to define the geometry of species, and build up a Z-matrix as calculation input file manually or using the computer program "CHEMSITE". Thermodynamic properties can be calculated by running computer program "MOPAC 6.0" with keyword "THERMO" and parameters (number of symmetry considered and number of internal rotors not included). The keyword "PRECISE" is usually used to set up a more strict criteria for the self-consistent-field (SCF) convergence in the geometry optimization process. Thermodynamic properties from MOPAC calculations then combine with some corrections for entropies and heat capacities. The most important one is the correction for entropy and heat capacity contributions from internal rotors. A computer program "VIBIR", developed by Bozzelli's group in NJIT, is used to obtain the value of entropy and heat capacity from internal rotors, which is not included in MOPAC calculations. This part of the contribution for entropy can account for up to 1/3 or 1/4 of total entropy of species. The

entropy contribution from optical isomers such as -OOH groups, is also combined to final result for specific species, a value of RLn2 is usually assigned to each of optical isomer.

1.3.2 Radicals

The calculations of thermodynamic properties of radicals are also based on radical's optimized geometry. The parent's geometry can be used with replacing H, which does not exist on radical, with dummy atom (X). The calculation should combine the keyword "UHF" (Unrestricted Hartree-Fock), especially for the calculations of open shell such as radicals. One more correction for entropy in addition to those for molecule is entropy contribution from electron spin (RLn2) because there is one unpaired electron on radical.

1.3.3 Transition States

The calculations of thermodynamic properties $H_{f,298}$, S_{298} and $C_p(T)$ of transition states are carried out by first defining the transition states using semi-empirical (MOPAC PM3) method. Thermodynamic properties as well as vibration frequencies, moments of inertia of transition states can then be calculated by adding the keyword "THERMO" with parameters (number of symmetry considered and number of internal rotors not included) to optimize geometric input files. The keywords "UHF" in addition "PRICISE" is often used.

There are different ways to find transition states for specific reactions. One of methods used in this study is to use the optimized geometry of reactant (radical or molecule), adjust certain bond length, bond angle or dihedral angle and use keyword "TS". The "SIGMA" or "NLLSQ" is used sometime to help find transition states. Identifying of a transition

state is usually carried by an image vibration frequency (with a minus sign) and reasonable internal atom distances in optimized geometry found. That the geometry will have no change after adding keyword "THERMO" is also helpful for identifying a transition state.

1.4 Thermodynamic Analysis

Thermodynamic analysis is carried out by computer program "THERMRXN" and "AFACT2F", developed by Bozzelli's group in NJIT. Based upon thermodynamic properties, $\Delta H_{f,298}$ S_{298} and $C_p(T)$ (T = 300, 400, 500, 600, 800, 1000 and 1500), thermodynamic analysis (THERMRXN) calculates thermodynamic properties for reaction such as ΔH_{rxn}, ΔU_{rxn}, ΔS_{rxn}, ΔG_{rxn}, and reaction equilibrium constant (K_c) or the ratio of forward Arrhenius A factor to reverse Arrhenius A factor (A_f/A_r) at temperature range from 298 to 1500 K. The ΔH_{rxn} and ΔU_{rxn} are used to calculate activation energies for isomerization reaction and unimolecular dissociation (elimination or beta scission) reactions based on activation energies for reverse addition reactions. Thermodynamic analysis (AFACT2F) can also calculate A factors in the form of $A'T^n$ using $\Delta S^{\neq}$ ($S_{reactant}$ - $S_{transition\ state}$) based on transition state theory. The fit value of A factor is also obtained from thermodynamic analysis for the temperature range from 300 K to 2000 K. Thermodynamic analysis also reports the temperature dependence of thermodynamic properties and shows negative temperature effects for some reactions.

CHAPTER 2

KINETICS

2.1 Types of Reaction on Kinetics Estimation

Many reactions are considered and covered in this study for modeling a real reaction system. Abstraction reactions are always the initial reaction and play key role in the low to intermediate temperature range. Thermal unimolecular dissociation and chemical activation addition reactions are the most important reactions considered in this study. Reaction to other new product channels as well as isomerization, stabilization and reverse reaction are included in this calculation. This is an important aspect of the reaction analysis for both combination as well as addition reactions that other modelers do not usually incorporate. This leads to a more correct treatment of fall-off and pressure dependence for these non-elementary reaction systems. Rate constants inclusion in for the model are obtained which incorporate the calculated pressure dependency and therefore make the model more fundamentally correct.

As for better organization of this thesis, we summarize several important reaction types here, including abstraction reaction (metathesis), addition reaction, elimination reaction (beta scission), isomerization reactions (especially unimolecular), simple dissociation reactions, and recombination reactions.

2.1.1 Abstraction Reactions (Metathesis)

Abstraction reaction rate constants are not pressure dependent and usually taken from evaluated literature when available. If estimation is required, a generic reaction is utilized

as a model and adjusted for steric effects. Evans Polanyi analysis is used on the reaction in the exothermic direction to estimate the energy of activation (E_a) for rate constant. An Evan Polanyi plot, E_a versus ΔH_{rxn}, allows use of a known ΔH_{rxn} to obtain E_a for these reactions. The abstraction reaction in an endothermic reaction must incorporate the ΔH_{rxn}, or thermodynamics will be violated.

When no literature data are available, an alternative estimation procedure from Dean and Bozzelli [11] is also used in this study but limited to abstraction by H, O, OH, NH_2 and CH_3. This estimation procedure is based on a reference reaction. For example, for abstraction by H to form a carbon-centered radical, the reaction $C_2H_6 + H \rightarrow C_2H_5 + H_2$ serves as a reference reaction with a well known rate constant taken from literature. Rate constant is expressed in modified Arrhenius form:

$$k = n_H A T^n \exp(-E_a/RT) = n_H A T^n \exp\{-[E_0 - f(\Delta H_0 - \Delta H)]/RT\} \text{ cm}^3\text{-mol}^{-1}\text{-s}^{-1}$$

Where n_H is the number of hydrogen atoms which can be abstracted from molecule, E_0 is the activation energy for reference reaction, ΔH_0 and ΔH are reaction heat formations for specific abstraction reaction and reference reaction respectively. The f is a fraction assigned by authors from several set of calculated value fitted to literature data. The A, n, f, E_0 and ΔH_0 as a reference value is list below.

R	A	n	E_0 (kcal-mol^{-1})	ΔH_0 (kcal-mol^{-1})	f
H	2.4×10^8	1.5	7.4	-3.1	0.65
O		1.5	5.8	-1.1	0.75
OH		2.0	0.86	-18.3	0.50
NH_2		1.94	7.2	-7.5	0.23
CH_3		1.87	10.6	-3.7	0.65

2.1.2 Addition Reactions

Addition reactions are treated with the quantum RRK formalism for k(E) and modified strong collision theory of Gilbert et al. for falloff. The QRRK analysis will be described in the following section. The reaction involves addition of an atom or radical to an unsaturated species. Addition reactions typically form an energized adduct with ca. 20 to 50 kcal-mol^{-1} of energy above the ground state. This energy is often sufficient to allow the adduct to react to other reaction products (lower energy) before stabilization occurs.

2.1.3 Elimination Reactions (Beta Scission)

These reactions are the reverse of addition reactions and utilize the quantum RRK formalism for k(E) and modified strong collision theory of Gilbert et al. for falloff and are treated in two ways. In the first way, a unimolecular quantum RRK formalism for k(E) and modified strong collision theory of Gilbert et al. for falloff is employed where reverse high-pressure reaction (addition) parameters are determined. The corresponding high-pressure unimolecular beta scission rate constants using microscopic reversibility are then calculated. These high pressure unimolecular elimination parameters are then input to the QRRK formalism to calculate the rate constants at the appropriate pressure. An alternate method is to use the reverse rate constants from the QRRK - modified strong collision reaction calculations for the corresponding addition reaction.

2.1.4 Isomerization Reactions (Special Unimolecular)

This reaction represents intramolecular, endothermic transfer of a H atom from a primary methyl carbon atom to the peroxy O radical. The activation energy (E_a) for the forward

rate of this reaction was estimated using the calculations, from analysis of the ethyl $+O_2$ reaction [12], and more recent comparisons to the experimental and calculation data base for this ethyl system. The data utilize:

E_a = Ring strain + E_{abst} + ΔH_{rxn}

where ΔH_{rxn} is the enthalpy of reaction (only included if reaction is endothermic). The ring strains are 28.0, 26.0, 6.0, 1.0 or 0, and 6.0 kcal-mol^{-1} for rings containing three, four, five, six, and seven members, respectively. Energies of abstraction E_{abst} are taken from Evans Polanyi plots of carbon atoms abstracting a hydrogen, where a abstraction by carbon atom is the reverse reaction in this system. These compared to an E_a of 12.5 kcal-mol^{-1} for a thermo neutral reaction and a decrease in E_a of 0.33 kcal-mol^{-1} for each 1 kcal in exothermicity.

Pre-exponential factors (A factors) for the ROO isomerization (unimolecular reaction) were obtained using Transition State Theory (TST):

$A(T) = (ek/h) \exp(\Delta S^{\neq}(T)/R)$ in AT^n form

where $\Delta S^{\neq}$ is calculated from $S^{\neq}_{(transition\ state)} - S_{(reactants)}$ which is obtained from semi-empirical calculation (MOPAC PM3) modified with entropy S(T) contributions from the internal rotors, electron spin of radicals and correction for optimal isomers, or from empirical estimations, which consider the number of lost rotors, and each rotor account for -4.3 kcal-mol^{-1}.

2.1.5 Dissociation Reactions (Simple Unimolecular)

Simple unimolecular (dissociation) reactions are the reverse of two radical recombination reactions. The rate constants are determined by two methods similar to beta scission reactions. The reverse high-pressure reaction (combination) parameters are determined. The corresponding high-pressure unimolecular dissociation rate constants are then calculated using microscopic reversibility. These high pressure unimolecular dissociation parameters are then input to the QRRK formalism to calculate the rate constants at the appropriate pressure and temperature. The reverse rate constant from the QRRK combination reaction calculation can also be used for the respective reaction.

2.1.6 Combination Reactions

These reactions involve the combination of two radicals or an atom with a radical. The energy of the adduct formed before stabilization is equal to the bond energy of the new bond(s) formed and this is typically on the order of 80 to 120 kcal-mol^{-1}. This is often sufficient under combustion conditions for an adduct, with this initial energy above its ground state energy, to react to lower energy products before stabilization occurs. The high pressure limit rate constant for combination is obtained from literature or estimated from known generic combination reactions. The QRRK chemical activation formalism is then used to calculate the rate constants at the appropriate pressure and temperature to all the recognized available channels.

2.2 Quantum RRK Calculations

Quantum RRK calculations are performed, through the whole study, to evaluate energy dependent rate constants, k(E), of the adduct to the various channels for the calculations

of branching ratios of the adduct formed from combination, addition or insertion reactions to various product channels. The RRK theory is then outlined below.

2.2.1 RRK Theory

Most modern theories of unimolecular reaction rates, including the Slater theory, the RRK (Rice and Ramsperger and Kassel) theory and the RRKM (Marcus Rice) theory, are based on the fundamental Lindemann mechanism involving collision energization of the reactant molecules, and more specifically on Hinshelwood's development of the original treatment.

The Slater theory [13-14]is a dynamical theory concerned with the detailed treatment of molecular vibrations and the behavior of particular molecular coordinates as a function of time. Reaction is postulated to occur in Slater theory when a chosen coordinate achieves a critical extension by the phase-coincidence of certain modes of vibration. The rate constant of energized molecule dissociation to product(s) (k_a) is related to a "specific dissociation probability" L; this is the frequency with which a chosen coordinate in the molecule reaches a critical value, and can be calculated for the case in which the vibrations of the molecule are assumed to be harmonic. The L is actually a function of the energies in the individual oscillators and not simply of the total energy E of the molecule.

In RRK theory the assumption is made that the rate of conversion of energized molecules into products is related to the chance that the critical energy E_0 is concentrated in one part of the molecule, e.g. in one oscillator (Kassel theory) or in one squared term (Rice-Ramsperger theory). This probability is clearly a function of the total energy E of the energized molecule.

The Marcus Rice theory, is known as RRKM theory since its basic model is RRK model. The main developments are the calculation of the rate constant of energization by quantum-statistical mechanisms and the application of ideas related to the Absolute Rate Theory for the calculation of the rate of conversion of energized molecules into products.

2.2.1.1 Lindemann-Hinshelwood Mechanism for Unimolecular Reactions

The theory known as Lindemann theory forms the basis for all modern theories of unimolecular reactions and has been developed from ideas published almost simultaneously by Lindemann [15] and Christiansen [16]. The main concept is that: (a) by collision, a certain fraction of the molecules become energized, i.e. gain energy in excess of a critical quantity E_0. The rate of the energization process depends upon the rate of bimolecular collision. (b) energized molecules are de-energized by collision, which is a reverse reaction. This de-energized rate is taken to be energy-independent and is equated with the collision number Z_2 by assuming that every collision of A^* leads to a de-energized start. (c) there is a time-lag between the energization and unimolecular dissociation or isomerization of the energized molecules. This unimolecular dissociation also occurs with a rate constant k_3 independent of the energy content of A^*. The whole idea can be expressed by the following equations.

$$A + M \rightarrow A^* + M \qquad (k_1)$$

$$A^* + M \rightarrow A + M \qquad (k_2)$$

$$A^* \rightarrow B + C \qquad (k_3)$$

where M can represent a product molecule, an added "inert" gas molecule, or a second molecule of reactant. In the simple Lindemann theory k_1, along with k_2 and k_3 is taken to be energy-independent and is calculated from the simple collision theory equation.

By application of the steady-state hypothesis to the concentration of A^*, the unimolecular rate constant and high pressure limit and low pressure limit rate and rate constants are then given as following:

High pressure limit rate $\quad \nu_\infty = (k_1k_3/k_2)[A] = k_\infty[A]$

Low pressure limit rate $\quad \nu_0 = \nu_{bim} = k_1[A][M] = k_{bim}[A][M]$

Unimolecular rate constant $\quad k_{uni} = (k_1k_3/k_2)/ (1 + k_3 /k_2[M]) = k_\infty / (1 + k_\infty /k_1p)$

Fall-off $\quad k_{uni}/ k_\infty = 1 / (1 + k_\infty /k_1p)$

One can expect that the Lindemann theory predicts a change in the order of the initial rate of a unimolecular reaction with respect to concentration at low pressure.

The k_1 in original Lindemann theory is taken from the collision theory expression ($k_1 = Z_1\exp(-E_0/kT)$ with $Z_1 = (\sigma_d^2N_A/R)(8\pi N_Ak/\mu)^{1/2}(1/T)^{1/2}$, where Z_1 will be in $Torr^{-1}$-s^{-1} (consistent with [M] in Torr and k_3 in s^{-1}) when σ_d = collision diameter in cm; μ = reduced molar mass in $g\text{-}mol^{-1} = (1/M_A + 1/M_B)^{-1}$; T = temperature in K; $N_A = 6.0225 \times 10^{23}\ mol^{-1}$; $R = 6.2326 \times 10^4\ cm^3\text{-}Torr\text{-}K^{-1}\text{-}mol^{-1}$; $k = 1.3805 \times 10^{-16}\ erg\text{-}K^{-1}$.

Based on the Lindemann's suggestion that k_1 could be increased by assuming that the required energy (energize molecules) could be drawn in part from the internal degrees of freedom (mainly vibration) of the reactant molecule, Hinshelwood [17] increases k^1 by using a much higher chance of a molecule possessing total energy $\geq E_0$ in s classical degrees of freedom, $(E_0/kT)^{s-1}\exp(-E_0/kT)/(s-1)!$, than one, $\exp(-E_0/kT)$ Lindemann used.

So the $k_1 = [Z_1/(s-1)!](E_0/kT)^{s-1}\exp(-E_0/kT)$ with k_1 a function of energy and replace k_1 and A^* as $k_{1(E\rightarrow E-\delta E)}$ and $A^*_{(E\rightarrow E-\delta E)}$ in mechanism above.

2.2.1.2 RRK Theory of Unimolecular Reactions

In order to make accurate quantitative predictions of the fall-off behavior of a unimolecular reaction it is essential to take into account the energy dependence of the rate constant k_a (k_3) for the conversion of energized molecules into activated complexes and hence products. One of accepted theories is the RRK theory, a statistical theory used in this thesis because it is more computable and needed parameters are readily obtained.

The RRK theory due to Rice and Ramsperger [18] and Kassel [19-20] was developed virtually simultaneously and very similar in their approach. Both consider that for reaction to occur a critical energy E_0 must become concentrated in one part of the molecule. They used the basic Lindemann-Hinshelwood mechanism of collision energization and de-energization, but assume more realistically that the rate constant of conversion of an energized molecule to products is proportional to a specific probability, a finite statistical probability that E_0 will be found in the relevant part of the energized molecule which contains E greater than E_0 since E of the molecule under consideration is assumed to be rapidly redistributed around the molecule. Obviously this probability will increase with E and make k_a a function of its energy content.

The difference between these two models is twofold. Firstly, Rice and Ramsperger used classical statistical mechanics throughout, while Kassel used classical method but also developed a quantum treatment; the latter is very much more realistic and accurate. Secondly, different assumptions were made about the part of the molecule into which the

critical energy E_0 has to be concentrated. The Kassel's model seems slightly more realistic by assuming the energy had to be concentrated into one oscillator. The quantum version of the Kassel theory serves as a theoretical basis for calculation performed in this thesis. The mechanism of RRK theory is written as:

$A + M \Leftrightarrow A^*_{(E \to E-\delta E)} + M \qquad \delta k_{1(E \to E-\delta E)}/k_2$

$A^*_{(E)} \rightarrow$ Products $\qquad k_a(E)$

The quantum version of version of Kassel's theory is based on the calculation of the probability that a system of s quantum oscillators, while the classical version considered s classical oscillators, with total energy E should have energy $\geq E_0$ in one chosen oscillator. It assume that there are s identical quantum oscillators, all having frequencies ν and hence energy $h\nu$, and so the critical energy E_0 is expressed as the critical number of quanta being $m = E_0/h\nu$, and the energy E of energized molecule is expressed as a total of n quanta with $n = E/h\nu$. The probability of that one oscillator contains at least m quanta, probability (energy $\geq$ m quanta in one chosen oscillator) is then equal to:

$$\text{Probability (energy} \geq \text{ m quanta in one chosen oscillator)} = \frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!}$$

Hence,

$$k_a(nh\upsilon) = A\frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!}$$

where A is proportion constant here and actually the same as the classical one.

Corresponding $k_1(E)$ of Hinshelwood expression is derived, refereed to energization into a specific quantum state rather than into an energy range E to E+δE, as

$$k_1(nh\upsilon) = k_\infty \alpha^s (1-\alpha)^{n+1} \frac{(n+s-1)!}{n!(s-1)!}$$

where $\alpha = \exp(-h\nu/kT)$.

2.2.1.3 Chemically Activation Reactions

Molecules undergo thermal unimolecular reactions as a result of energization by molecular collision. This molecular collision at a given temperature produces energized molecules with an equilibrium distribution of energy which enables the fraction of molecules energized into a particular energy range or quantum state. The energization methods other than by molecular collision, such as photoactivation and chemical activation, may produce a non- equilibrium situation in which molecules acquire energies far in excess of the average thermal energy. This amount of excess of energy contained in energized adduct makes chemical activation reactions much more important in a particular system, and a much different treatment for the rate of conversion decomposition of energized adduct to product (including back to reactant) which is very competing with the rate of its collision stabilization.

A example of chemically activated reaction system is neopentyl radical + O_2 system. As we will discussed in part II, C3CC. radical reacts with O_2 to form a chemically activated, energized adduct [C3CCOO.*], this process of forming adduct is much more efficient than that by thermal molecular collision, and adduct contains excess energy from the chemical reaction. The energized adduct [C3CCOO.*] could go back to reactant C3CC. + O_2, or could directly go to products C2CyCCOC + OH via a intramolecular H shift. The QRRK calculation (see chapter 4 in part II) shows that the chemical activation process is more

important than thermal dissociation process. Another example of chemically activated reaction system is the addition reaction of OH to unsaturated double in iso-butene (C2C=C). The channel of forming a chemically activated adduct $[C2C=C\text{--}OH]^{\bullet}$ followed by a dissociation to various products is an important pathway in iso-butene oxidation system to explain product distribution and this chemical activation channel is very competing with abstraction reaction.

The basic idea of the treatment of a chemical activation system is that a vibration excited molecule $A^{\bullet}$ by an association of reactants can reform reactants with a rate constant $k'_a(E)$, form decomposition products with a rate constant $k_a(E)$ or be de-energized to stable molecules A.

On the strong collision assumption the first order rate constant for de-energization is equal to the collision frequency, $\omega = Zp$ where p is the total pressure and Z is collision number (see "2.2.1.1 Lindemann-Hinshelwood Mechanism for Unimolecular Reactions" on page 19).

Suppose that the fraction of molecules which are energized per unit time into the energy range between E and E+δE is $f(E)\delta E$. To simplify, one can consider only one decomposition path (back to reactant can be considered as one of decomposition paths), then the fraction of $A^{\bullet}$ decomposing (say path D) compared with those stabilized (say path S) is $k_a(E)/[k_a(E)+\omega]$. The fraction of molecules in the energy range between E and E+δE decomposing to products is therefore $\{k_a(E)/[k_a(E)+\omega]\}f(E)\delta E$, and the total number of molecules decomposing per unit time (D), at all energies above the critical energy E_0, is:

$$D = \int_{E_0}^{\infty} \frac{k_a(E)}{k_a(E) + \omega} f(E)dE$$

corresponding, the total rate of stabilization (S) is:

$$S = \int_{E_0}^{\infty} \frac{\omega}{k_a(E) + \omega} f(E)dE$$

Considering an average rate constant $<k_a>$ for all energies above E_0, there have:

$$\frac{< k_a >}{\omega} = \frac{D}{S} = \frac{\text{No. molecules decomposing per unit time}}{\text{No. of molecules being stabilized per unit time}}$$

So,

$$< k_a >= \omega \frac{\int_{E_0}^{\infty} \{k_a(E) / [k_a(E) + \omega]\} f(E)dE}{\int_{E_0}^{\infty} \{\omega / [k_a(E) + \omega]\} f(E)dE}$$

The $f(E)$ is the distribution function of energized molecules in the energy range between E and E+δE. In the thermal energization systems, this distribution function is simply the thermal quantum Boltzmann distribution $K(E)$ and the rate of energization into the energy range between E and E+δE is $K(E)\delta E = \delta k_1/k_2$. For the chemically activated system described here, the distribution function can be derived by applying the principle of detailed balancing to the reverse process to reactants. Consider a situation in which the processes D and S can be ignored and equilibrium is established between A^* and reactants, then the fraction of molecules with energy between E and E+δE is Boltzmann distribution $K(E)\delta E$, so the rate of dissociation to reactants is then $K'_a(E)K(E)\delta E$, and by the principle of detailed balancing this also gives the rate of combination of reactants to give A^* in this energy range. The total rate of energization to all levels above the minimum energy E_{min} (the minimum energy of A^*) is:

$$\text{Total rate of energization} = \int_{E_0}^{\infty} k'_a(E)K(E)dE$$

Therefore, the distribution function is given by:

$$f(E)\delta E = \frac{k'_a(E)K(E)\delta E}{\int_{E_0}^{\infty} k'_a(E)K(E)dE}$$

The $f(E)\delta E$ can be incorporated into QRRK theory for $k_a(E)$ and $k_1(E)$ (see "2.2.1.2 RRK Theory of Unimolecular Reactions on page 21) serves as a basis for the calculations for chemical activation reaction systems.

2.2.2 QRRK Analysis for Unimolecular and Chemical Activation Reactions

QRRK analysis, as initially presented by Dean [21 - 23] combined with the modified strong collision approach of Gilbert et al [24], are used to compute rate constants for both chemical activation and unimolecular reactions, over a range of temperature and pressure. The computer program CHEMDIS, based on the QRRK theory outlined as above, and unimolecular dissociation and chemical activation formalism carries out all unimolecular and chemical activation reactions involved in this thesis. The input parameters for CHEMDIS are: (1) High pressure limit rate constants (Arrhenius A factor and activation energy E_a) for each reaction included for analysis; (2) A reduced set of three vibration frequencies and their associated degeneracy; (3) Lennard-Jones transport parameters, (s (Angstroms) and e/k (Kelvin)), and (4) molecular weight of well species. All these input parameters are readily available or straightforward to estimate.

2.2.2.1 Input Data Requirements for the QRRK Calculations

It is important to have accurate input data for the calculations, without this aspect the accuracy or assumption in the calculations of fall-off or chemical activation rate constants are of less value.

Pre-exponential factors (Arrhenius A factors) in the high pressure limits, are obtained from calculations and the literature or are estimated from generic reactions for combinations and additions. Transition state theory is utilized for isomerization using the methods Benson [25] and Dean [21].

Activation energies come from endothermicity of reaction ΔU_{rxn} and from analogy to similar reactions with known energetics.

A reduced set of three vibration frequencies and their associated degeneracy are computed from fits to heat capacity data, as described by Ritter [2]. These have been shown by Ritter to accurately reproduce molecular heat capacities, Cp(T), and by Bozzelli et al [26] to yield accurate density of states r(E) to partition coefficient (Q) ratios.

Lennard-Jones transport parameters, s (Angstroms) and e/k (Kelvin), are obtained from tabulations [27] and from a calculation method based on molar volumes and compressibility [28]. The calculation formula is: $\sigma = (2.3551\text{-}0.087w)/(P_c/T_c)^{1/3}$ and $\varepsilon/\kappa = (0.7915+0.1693w)T_c$, where w is molecular weight in gram-mol^{-1}, P_c and T_c are the critical temperature and the critical pressure respectively.

Arrhenius A factors for the radical bimolecular combination at the high pressure limit are obtained from literature, and from trends in homologous series of these type reactions. When necessary, estimation is done in a consistent and uniform manner with reference to

literature, experiment and / or calculation in all cases. The input parameters and references are important, and data are listed in the tables associated with each calculation.

2.2.2.2 Modifications

A significant number of modifications have been made since the initial descriptions of the quantum RRK and fall-off calculations were published [21 - 24]. These modifications [23] include:

- Use of a manifold of three vibration frequencies and respective degeneracy, plus incorporation of energies from one external rotation mode for the calculation of the ratio of the density of states to the partition coefficient $\rho(E)/Q(T)$ and for calculation of $k(E)$ and of $F(E)$.

- The F_E factor is now explicitly calculated for use in determining the collision efficiency β_c [24] in place of the previously assigned 1.15 value. The β_c is calculated from Gilbert et. al. eqn. 4.7 [24].

- The Lennard-Jones collision frequency Z_{LJ} is calculated by: $Z_{LJ} \equiv Z\ \Omega^{(2,2)}$ integral [27, 29, 30], Ω is obtained from fit of Reid et al [27].

The QRRK analysis with the modified strong collision approach and constant FE for fall-off has been used to analyze a variety of chemical activation reaction systems [31 - 40]. It is shown to yield reasonable results in these applications; and provides a mechanism by which the effects of temperature and pressure can be evaluated and included in the kinetics.

Chebyshev polynomials (7×3) incorporate the pressure and temperature dependence into rate constant expression. A modified Chemkin Interpreter is used to incorporate the combined pressure and temperature dependent rate expression into the Chemkin intergrators.

PART II

MODELING STUDY ON THE NEOPENTYL RADICAL + O_2 REACTION SYSTEM

CHAPTER 3

INTRODUCTION

3.1 Overview

Atmospheric and combustion reactions forming alkyl radicals are well-characterized relative to the subsequent reactions of the alkyl radicals with O_2. The reactions of alkyl radicals with O_2 are, however important and often rate limiting processes in the low temperature chemistry (below 1000 K) of hydrocarbons oxidation, especially the chemistry which occurs prior to ignition in internal combustion engines and cool flames. The reaction processes are, unfortunately, relatively complex and the analysis presents a source of some controversy [41-42]. This oxidation process involves formation of a peroxy radical, which contains ca 35 kcal-mole^{-1} of excess internal energy, this can either be lost via collision process or used for further reaction (including dissociation back to reactants) before stabilization occurs [31,43].

The overall reaction of alkyl radicals with O_2 to form the conjugate alkene plus HO_2 is considered the dominate process over the temperature range 500 to 900 K; it is often treated as one step by many modelers [44-45]. There is, however, a significant quantity of data from the elementary kinetics community which shows (for the reaction systems studied) that the reactions occur by formation of a peroxy adduct, which undergoes a unimolecular isomerization and the hydroperoxy alkyl isomer undergoes further reactions to products. While this reaction process is more complex due to pressure dependent stabilization channels, proper inclusion of it in kinetic models for combustion processes will make them more accurate and meaningful for use in optimization. It will, in addition,

extend their range of validity. For example, it is the subsequent reactions of the alkyl peroxy radical intermediate that are determinated essential, by combustion modelers, to predict negative temperature coefficient behavior [41,46].

Two features of neopentane facilitate a simpler interpretation of results, relative to most alkyl radical - oxygen reaction systems. (i) All the C-H bonds are identical so that only one species of alkyl radical is involved. (ii) The carbon atom radical site is connected to a carbon with no hydrogen atoms, thus, unlike the majority of alkyl radicals, the formation of the conjugate alkene by a more direct abstraction of H by O_2, not involving radical isomerization, is structurally impossible. Reactions of stabilization, reverse dissociation, isomerization and isomer decomposition are dominant here.

Only few studies focus on reactions of neopentane + O_2 system, and the basic reaction scheme expressed as following:

R3-1	C3CC. → C2C=C + CH_3
R3-2	C3CC. + O_2 → C3CCOO.
R3-3	C3CCOO. → C3.CCOOH
R3-4(a)	C3.CCOOH → C2CyCCOC + OH
R3-4(b)	C3.CCOOH → C2C=C + C.H_2OOH
R3-5	C3.CCOOH + O_2 → Products

The fundamental chemical kinetic study of neopentane and/or neopentyl radical will certainly help to understand fundamental chemistry of combustion at the low and intermediate temperatures. Only one full mechanism exists for oxidation of neopentane by Curran (see 3.4 Literature Review starting on page 34), but it is too complex with about 1570 reactions included, few of which account for fall-off, and it may not be used as sub-mechanism in the other model. So, it's really make sense for us to build a reduced but more accurate mechanism for neopentane combustion under the intermediate temperature.

3.2 Objective of this Study

- Development and advancement of the understanding of the reaction of neopentyl + O_2 system under intermediate temperature conditions.
- Identification of important reactions and key species in the intermediate temperature chemistry of neopentyl + O_2 system.
- Development of a reduced kinetics model for neopentyl + O_2 system, based on thermochemical kinetic principles, supported by literature data. Particular importance will be directed to reactions of primary radical intermediates with O_2, plus and OH addition reactions to olefins and carbonyl species, and then subsequent reactions of these radical adducts with O_2.

3.3 General Approach

The reaction mechanism is based upon fundamental principles of thermochemical kinetics including Transition State Theory (TST), and accurate molecular thermodynamic properties. The mechanism consists of elementary reactions with each reaction based on literature evaluation, or if it is estimated, on thermochemical kinetics principles.

Chemical activation analysis to determine rate constants as a function of temperature and pressure will be performed on combination reactions of radical intermediates with O_2 and on radical (OH) addition to unsaturated species, olefins and carbonyls. Unimolecular dissociation analysis will be performed to determine temperature and pressure dependence, especially fall-off, for beta scission and important unimolecular decomposition reactions.

Quantum Kassel Analysis (see part I) is also utilized to account for fall-off effects in unimolecular reactions and in chemical activation processes such as addition or combination reactions. We apply this analysis to rate constants which are pressure dependent that are reported in the literature from measurements at other pressures. as well as our estimated rate constants for these type of reactions.

The reaction mechanism consisting of all involved elementary reactions will finally be validated by experimental results or literature data and therefore be used to predict product distribution for experimental or real chemical reaction systems by performing special species concentrations interpretation by some computer programs.

3.4 Literature Review

Over 70% of these studies was focused on abstraction reactions of hydrogen from neopentane by OH, CH_3, Cl, O, H, CH_3O, CN, $(CH_3)_3CH_2O$, C_2H_5, D, Br, F, CD_2, NF_2, CF_3,CH_3CHCH_3, CH, CD_3, C_2D_5 and NH_2. Most groups interested in radical abstraction reactions from alkane and tried to obtain bimolecular rate constants for one particular reaction or a series of abstraction reactions with experimental or theoretical studies.

The previous important studies which focused on neopentane goes in two ways, one of which is the neopentane pyrolysis reactions and unimolecular decomposition of neopentyl radical, the other focused on the oxidation reactions of neopentyl radical by few groups.

There were three studies specialized on the unimolecular decomposition of neopentyl radical, (R1) which is an important competitive reaction in the oxidation environment in the intermediate temperature range.

Anderson and Benson [47] investigated the reaction R3-1 in a study of the pyrolysis of neopentane in the presence and absence of HCl at 489 °C and gave an initial rate, $k_1 = 10^{3.3\pm.03}$ s^{-1} and $E_a = 17.0 \pm 0.2$ kcal-mol^{-1} from the rate. It is a pretty low rate compared to later studies.

Furimsky and Laidler [48] studied unimolecular decomposition of neopentyl radical (R3-1), during their experimental and kinetics study on the mercury-photosensitized decomposition of neopentane over the temperature range 230-335 °C and at pressures from 3 to 280 Torr. They obtained a high pressure limit rate constant, $k_\infty = 2.5\times10^{13}\exp(-29.0/RT)$ s^{-1}, directly based on rate constants for the abstraction reaction between CH_3 radicals and neopentane and for the combination of CH_3 radicals with t-C_4H_9 radicals. They also found the fall-off at low pressures ($P_{neopentyl} < 2$ Torr) and a low pressure limit rate constant, $k^0 = 5.8 \times 10^{10}$ exp (-17.1/RT) ml-mol^{-1}-s^{-1}.

About 20 years later, Slagle et al [49] studied the loss of neopentyl radical using a heated tubular reactor coupled to a photoionization mass spectrometer over a 1 to 10 Torr pressure range and a 287 to 377 °C temperature range. They produced neopentyl radical indirectly by pulsed excimer laser photolysis of CCl_4 (to produce CCl_3 + Cl) followed by the rapid reaction between the Cl atoms and neopentane to produce neo-C_5H_{11} + HCl. Neo-C_5H_{12} concentrations were high enough to "convert" the Cl atoms to neo-C_5H_{11} radicals within 0.5 ms and neo-C_5H_{11} concentrations were low (typically in the range (1-6) $\times 10^{10}$ molecules cm^{-3}). This was achieved by selecting the initial conditions (CCl_4 concentration and laser intensity) so that reactions between photolysis products (including the C_5H_{11} + C_5H_{11} recombination reaction) had negligible rates compared to that of the

unimolecular decomposition process under study. They monitored decomposition of neo-C_5H_{11} radical at various temperatures (287 to 377 °C) allowing an enthalpy of reaction to be derived. Unimolecular rate constants were determined as a function of bath gas (He, N_2 and Ar), temperature and bath gas densities ((3-30) × 10^{16} moleculaes-cm^{-3} for He and (6-12) × 10^{16} moleculaes-cm^{-3} for N_2 and Ar). They modeled (RRKM) the unimolecular decomposition of neo-C_5H_{11} to iso-butene + methyl radical and determined a (30.9 ± 1.0) kcal-$mole^{-1}$ barrier and an A factor of $10^{13.9\pm0.5}$ (7.94×10^{13}), both the E_a and A factor compare well with data obtained by Baldwin [50] and Furimsky [48].

More recently, Mitchell and Benson [51] conducted a modeling study of the neopentane pyrolysis and reinvestigated unimolecular decomposition of neopentyl radical with the aid of computer simulation and sensitivity analysis techniques, over the temperature range of 477 to 527 °C (750 to 800 K) in the absence and presence of additives iso-butene, HCl and HBr. They concluded that the apparent discrepancy between Anderson et al [47] and other reports [48-49 50] for reaction R3-1 is due to the use of an incomplete mechanism in the former determination. The experimental data from Anderson et al [47] are fully consistent with the use of a k_1 value determined by Slagle et al [49] when the data are interpreted using their more detailed mechanism.

The research group of Bayes et al [52-53] was focusing on kinetics of the initial neopentyl peroxy radical formation at low pressure and on the equilibrium and thermodynamic aspects of the oxygen addition reaction. They studied the rate constants on reaction of neopentyl radical with O_2 (R3-2) at 266 to 374 K and low pressure, 3 to 3.5 Torr. They monitored the pseudo-first-order decay of the neopentyl radicals as a function of oxygen,

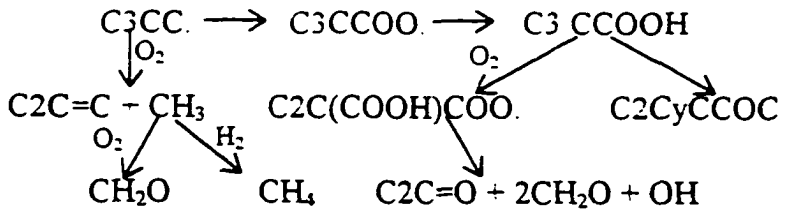
using a mass spectrometer as a detector. Neopentyl radicals were produced by the laser flash photolysis of neopentyl bromide using an ArF laser at 193 nm, or by the two step method described above in Slagle's experiment (first, chlorine atom, then neopentyl radicals)[49]. Their experimental results show a negative temperature dependence for the rate constant of neopentyl radical with O_2. They used adiabatic channel model calculation to interpret their results and reported the rate constant of this reaction as $k = \{2.1 \times 10^{-12}$ cm^3 $molecules^{-1}$ $s^{-1}\}(T/300\ K)^{-(2.1\pm0.4)}$, with no fall-off analysis.

Hughes et al [54] conducted a direct measurements of the neopentyl -peroxy-hydroperoxy radical isomerization (R3-3). They studied the formation of OH radical from thermal decomposition of neopentyl iodide in a bath of He with varied concentrations of O_2 at pressures of 575 to 660 Torr and at temperatures from 660 to 750 K. OH radical product concentration profile versus time was monitored and fit to bi-exponential growth curves. An exact analytical solution was postulated incorporating peroxy formation, reverse dissociation, isomerization (hydrogen atom transfer, but non-reversible), and only one isomer decomposition product channel – cyclic ether + OH. Hughes et al concluded that the above reaction processes were the only important components to include in their analysis, that the isomerization process had the barrier controlling the overall reaction process(es) and that the kinetics and pathways for adduct formation, reverse decomposition, isomerization and subsequent hydroperoxide alkyl radical decomposition were in good agreement with previous studies of the Baldwin and Walker research group [50]. Hughes et al reported rate constants for the isomerization with A of 1.58×10^{12} and E_a of 29 kcal $mole^{-1}$, where the E_a is needed to correlate with a combined ring strain plus E_a abstraction of 17 kcal $mole^{-1}$.

Except above studies on individual reaction involved in the oxidation of neopentyl radical, there were several investigations on the oxidation of neopentane or neopentyl radical by few groups.

The earliest investigations on the oxidation of neopentane or neopentyl radical were conducted by several workers [55 - 59] over the temperature range 260 - 350 °C. Zeelenberg [55] examined the products formed during the very early stages of reaction at 260 °C, but reported results for only one mixture composition. Antonik and Lucquin [56-57] studied the cool flame and explosion limits, and carried out a partial analysis of the products in the presence and absence of HBr at 298 °C. Drysdale and Norrish [58] determined the products over a wide extent of reaction at 280 °C, but the results were limited to one mixture and appear incomplete; for instance, the yield of the important product 3,3-dimethyloxetan was not given. Fish [59], in a study of the non-isothermal oxidation of neopentane at 300 - 350 °C, gave only a qualitative distribution of products. There were no or little mechanism and kinetic information reported in this early stage.

In 1970's, Baker et al [60 - 62] conducted a more completely experimental study on neopentyl radical by adding neopentane and the primary products to slowly reacting mixtures of hydrogen and oxygen at 480 °C, in a flow reactor (an aged boric-acid-coated Pyrex vessel) with reaction times ranging up to 200 seconds. They reported all products detected by colorimetry for formaldehyde and gas chromatography for all others under their experimental conditions and proposed a simple mechanism as follows to explain the formation of primary and secondary products.



Several years later, the same research group of Baldwin and Walker reworked on the oxidation reactions of neopentyl radical derived from neopentane in an atmosphere of hydrogen and oxygen at temperature range from 380 to 520 °C (653 to 793 K), in a flow reactor (an aged boric-acid-coated Pyrex vessel) with reaction times ranging up to several tens of seconds and gave the first complete experimental and kinetics study on the oxidation of neopentyl radical [50]. They analyzed stable products as a function of the concentration of oxygen at temperature from 380 to 520 °C (653 to 793 K) and analyzed the data using steady state and equilibrium relationships. They concluded that the reactions of neopentyl radicals in an oxidizing environment involve a relatively simple mechanism which gave a quantitative interpretation of the product yields; and that the only detectable initial products at their experimental temperature were 3,3-dimethyloxetan (DMO), acetone, iso-butene, and formaldehyde. They determined Arrhenius parameters for those elementary reactions included in their mechanism by extrapolating the product ratios ([acetone] + [DMO]) / [i-butene] and [acetone] / [DMO] which were measured using gas chromatograph coupled to an integrator at each temperature, and reported a $k_1 = 10^{13.65\pm0.2}$ exp (-127.4 ±6 kJ-mol^{-1}/RT) s^{-1} by thermochemical method for reaction R3-1; $k_2/k_{-2} = 2.7 \times 10^{-5}$ exp (+105.1 kJ-mol^{-1}/RT) dm^3-s^{-1} by using of Benson's additivity data [50] for reaction R3-2; $k_3 = 10^{13.08}$ exp (-120.0 ±6 kJ-mol^{-1}/RT) s^{-1} for reaction R3-3; $k_{4a} = 10^{11.30}$ exp (-73.0 kJ-mol^{-1}/RT) s^{-1} and $k_{4b} = 10^{13.65}$ exp (-116.0 kJ-mol^{-1}/RT) s^{-1} for

reaction R3-4(a) and R3-4(b). They also combined Arrhenius expressions for their 1,5p H-atom transfer (where p represents primary) in neopentyl peroxy radical and 1,4p H-atom transfer in ethyl peroxy radical [63], with thermochemical calculations to estimate a set of Arrhenius parameters for primary, secondary and tertiary intramolecular H-atom transfers in alkyl peroxy radicals involving 4 to 8 member cyclic transition states (at 753 K).

The only other complete study, which is a pure kinetics modeling study, on neopentane oxidation was conducted by Curran et al [64]. They have recently published a detailed chemical kinetic model to analyze experimental results, obtained by Baker et al [61-62], on the oxidation of neopentane in a closed reactor at 500 Torr pressure and one temperature, 480 °C (753 K). The important rate parameters in Curran's mechanism were based on empirical estimations and literature data. They used Slagle's data [49] for R1; Xi's data [53] for reaction R3-2. They calculated rate constant for isomerization reaction (R3-3) based on the theoretical methods of Bozzelli [41] and gave $k_3 = 10^{12.35}$ exp (-23.9 kcal-mol^{-1}/RT) s^{-1} for reaction R3-3; evaluated rate parameters for the cyclic ether formation reaction based on their earlier study [65] for the formation of oxetan species from an alkyl hydroperoxide radical and gave a $k_{4a} = 10^{10.40}$ exp (-15.25 kcal-mol^{-1}/RT) s^{-1} for reaction R3-4(a). Curran et al calculated rate constants for β-scission reaction by considering methyl radical addition to iso-butene and taking Slagle's data [49] for this reverse reaction and gave $k_{4b} = 10^{13.70}$ exp (-29.0 kcal-mol^{-1}/RT) s^{-1} for reaction R3-4(b). The rate constants model stable species profile well and are presented as part of a very large, - several thousand reactions, general hydrocarbon oxidation model. The paper developed detailed reaction paths, but with no calculations of transition state

thermochemical properties. no performance of fall-off analysis as a function of temperature and pressure for chemical activation or unimolecular reaction system.

CHAPTER 4

KINETIC MODELLING FOR THE NEO-C_5H_{11} + O_2 SYSTEM

4.1 Thermodynamic Properties

All species involved in the modeling mechanism have to have assigned thermodynamic parameters to support all reaction rate constant estimations or QRRK calculations and species concentration interpretations. Thermodynamic parameters ΔH_{f298}, S_{298} and $C_p(300)$ to $C_p(\text{infinity})$ for these species in the neopentyl radical + O_2 system are listed in Table IA. 1. The thermodynamic properties for the relevant radicals and stable parents were obtained by group additivity using THERM (see section "1.2 Group Additivities (THERM)" on page 4) with recently published peroxy groups and Hydrogen Bond Increment groups [66 - 68]. The OO symbol is a new group notation for peroxides, groups were developed using Ab Initio (Gaussian 94 6-31G** and MP2) and semi-empirical calculations on isodesmic reactions. The thermochemical data allow calculation of reverse reaction rate constants by microscopic reversibility [69]. Entropies and $C_p(T)$ values of radicals are from use of Hydrogen Bond Increments (HBI) [3]. The thermodynamic property entropy and heat capacity for species C3CCOO., C3.CCOOH and C2CyCCOC were calculated from semi-empirical calculation method MOPAC PM3 (see section "1.3 MOPAC on page 9) to consistent with corresponding reaction transition state calculations for reaction analysis.

4.2 Important Transition States

Three important transition states were defined and calculated for this modeling study system. Isomerization reaction of neopentyl peroxy radical (C3CCOO.) to neopentyl hydroperoxide radical (C3.CCOOH) had been combined into modeling mechanism, in totally different way from previous study, we consider this reaction as a faster-established equilibrium reaction (see section "5.3 Validation and Comparison with Literature Data), which does not affect the formation of OH radical a lot. Hughes et al [54] considered this reaction as rate control step and obtained a pretty high activation energy from their experimental result of the OH profile. The second important transition state defined in this neopentyl system is one of the cyclic compound, oxetan (C2CyCCOC), formation reaction from neopentyl hydroperoxide radical (C3.CCOOH). This is a OH elimination and cyclic compound formation reaction, which accounts for over 80% of OH formation while Hughes et al [54] used this reaction to account for all OH formation to obtain the rate constant for isomerization reaction. The last important transition state defined is for a beta scission of neopentyl hydroperoxide radical (C3.CCOOH) to iso-butene and methyl hydroperoxide radical (C.H_2OOH) which will rapidly dissociated to formaldehyde and OH radical. This reaction will account for part of total yield of iso-butene, a major product in neopentyl radical + O_2 system, this is the first try to use higher level calculation method to study this type of reaction and the detail will be discussed in chapter 10 of part IV on page 136.

Thermodynamic properties of transition states, related species and thermodynamic analysis are listed in TS IB. 1 and TS IB. 2. The S_{298} and $C_p(T)$ on transition states and relevant species calculated by using semi-empirical (MOPAC PM3) (see section 1.3 MOPAC).

Enthalpies of transition states are from evaluation of activation energies from kinetics. experiments and calculations in the literature on similar reactions. Enthalpies of relevant species are calculated from group additivity (THERM). Equilibrium constants $K_{eq}(T)$ are calculated from thermodynamic properties of reactants and products or reactants and transition states as a function of temperature. Reverse rate constants are calculated from $K_{eq}(T)$ and $k_f(T)$ values.

Semi-empirical (MOPAC PM3) calculations are also used to define transition state structures so provide bond distance information. These data are coupled into the QRRK fall-off calculations to determine the A factors as a function of temperature.

4.2.1 C3CCOO. → TS(1) → C3.CCOOH

The structure of transition state for isomerization of neopentyl peroxy radical (C3CCOO) to neopentyl hydroperoxide radical (C3.CCOOH), determined by semi-empirical (MOPAC PM3) calculation, is shown in TS IB. 3 along with frequencies, moments of inertia and barriers for internal rotors. TS IB. 4 and TS IB. 5 give the transition state's Z-matrix, containing bond angles and dihedral angles and the interatomic distances. TS IB. 3 shows that the breaking C-H bond stretches to 1.268 angstroms from 1.09 angstroms, and the forming O-H bond length is 1.292 angstroms which is longer than regular O-H bond length 0.95 angstroms.

TS IB. 2 shows temperature dependence of the properties of H transfer (isomerization) from thermodynamic analysis. Entropies of the reaction increase with temperature. The A factor increase with temperature, which indicate that transition state gets looser when temperature goes higher. E_a from this MOPAC calculation is usually larger than that from

the evaluation of kinetics, experiments and calculations in the literature on similar reactions. The latter one have been used in the studies.

4.2.2 C3.CCOOH → TS(2) → C2CyCCOC + OH

The structure of the transition state for this oxetan formation reaction along with frequencies, moments of inertia and barriers of internal rotors for transition state are shown in TS IB. 6. The breaking O-O bond length is 1.630 angstroms and the forming C-O bond length is 1.866 angstroms; 1.253 and 1.310 times longer than normal RO-O. and R-OO. bond lengths of 1.3008 and 1.4249 angstroms respectively [70].

A thermodynamic analysis (TS IB. 2) shows that $\Delta S^{\neq}(T)$ for this reaction decreases with temperature — negative temperature effect, thus on a relative scale, the transition state gets tighter with increased temperature.

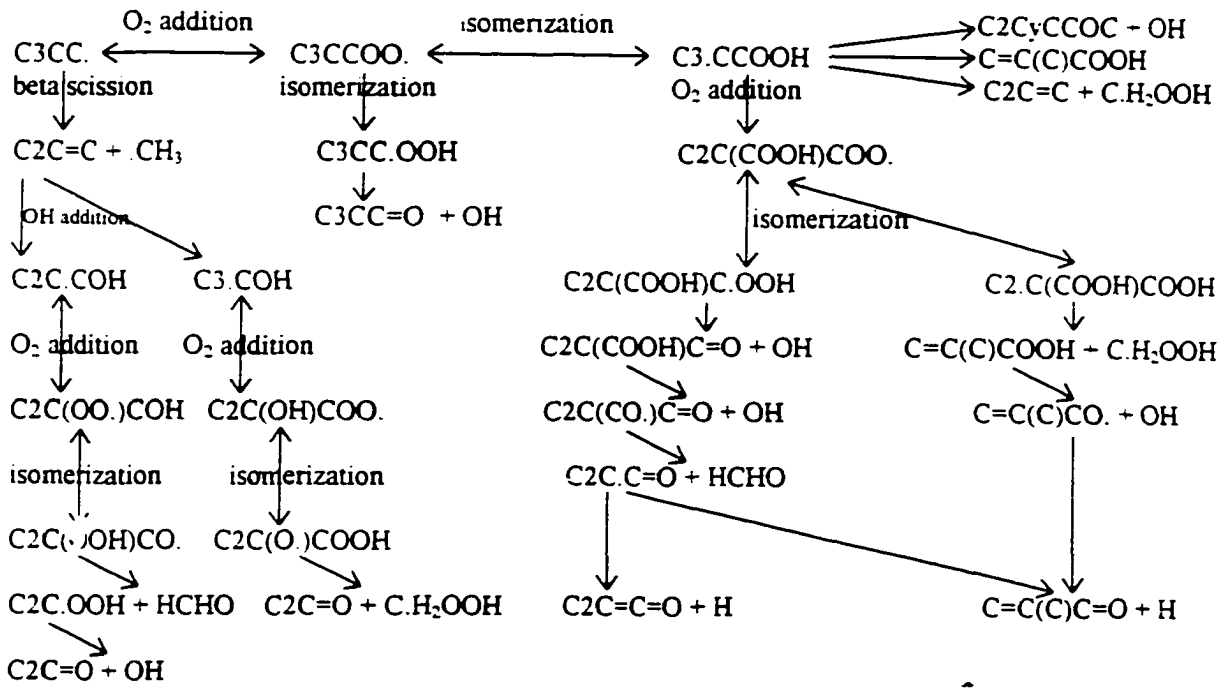
TS IB. 7 and TS IB. 8 show the transition state's Z-matrix, containing bond angles and dihedral angles and the interatomic distances.

4.2.3 C3CCOO. → TS(x) → C2C=C + C.H_2OOH

We could not find a transition state for this direct elimination channel. The reaction would have a carbon - hydrogen - oxygen bond being formed, and both a carbon and an oxygen leaving from a near planar iso-butene structure. We do not include this reaction in the analysis. If the reaction occurred the C.H_2OOH would rapidly form OH + CH_2O.

4.3 Quantum RRK Analysis

The elementary reaction mechanism of the neopentyl radical + O_2 system is outlined as:



There are several dominant pathways here. At the intermediate temperature, the unimolecular dissociation of neopentyl radical is very competitive with the addition of O_2 to it, which are two major pathways for neopentyl radical.

The O_2 addition reaction pathway accounts for the primary major products other than iso-butene such as oxetan (C2CyCCOC) and part of iso-butene. Treatment of the chemically energized complex reactions allows analysis of decomposition back to reactants, intramolecular transfer of hydrogen atoms to form hydroperoxy radicals which further decompose to primary and secondary products before stabilization to ground state peroxy or hydroperoxy radicals. Further reactions of the stabilized peroxy radicals include: dissociation to reactants, or isomerization to hydroperoxy via H shift and then beta scission to final products, or addition of a second O_2.

The unimolecular dissociation of neopentyl radical is certainly responsible for the production of most of iso-butene, whose further reactions, the attacking of OH and HO_2 radicals and then O_2 addition to hydroxide and hydroperoxide radicals, may account for many other secondary or minor products.

All reaction pathways of addition reactions and unimolecular isomerization or dissociation reactions are analyzed by construction of potential energy diagrams of the systems. and a assignment of sets of high pressure limit rate constants based on existing experimental data, literature data, theoretical calculation data, and on group additivity estimation techniques, thermodynamic analysis and chemical reaction microscopic reversibility. The most important reactions in this system, such as the reversible peroxy formation, the isomerization channels as well as the OH formation path, are discussed as follows.

4.3.1 Chemical Activation Reaction System: C3CC. + O_2 → Products

An energy level diagram of the pathway that the O_2 addition to neopentyl radical and subsequent dissociation reactions, and data for each high pressure limit rate constant are shown and listed in Appendix ID. 1. Reaction channels for the energized adduct C3CCOO.* include dissociation back to reactants, stabilization to C3CCOO., and isomerization via hydrogen transfer to hydroperoxide radical. The energized isomer C3.CCOOH* can undergoes cyclic ether formation to C2CyCCOC + OH, elimination (beta scission) to C=C(C)COOH + CH_3 and C2C=C + C.H_2OOH or stabilization to C3.CCOOH radical. The other energized isomer C3CC.OOH* will rapidly dissociate to C3CCHO + OH. The barrier for isomerization to C3.CCOOH is evaluated as 11.39 kcal-mol^{-1}, some lower than dissociation back to reactants (Appendix ID. 1). There is

sufficient energy in the adduct C3CCOO.* to allow isomerization to occur before it is stabilized – i.e. a chemically activated reaction path.

Figure IC. 1(a) shows the apparent rate constants for the product channels of C3CC. + O_2 versus temperature from 300 to 1300 K at atmospheric pressure. It shows that the dominant product channel for C3CC. + O_2 chemical activation pathways is stabilization to C3CCOO. (filled squares) at and below 800 K. When temperature rises above 800 K, the chemically activated unimolecular dissociation to isomer C3.CCOOH, products C2CyCCOC + OH, C2C=C + C.H_2OOH, C=C(C)COOH + .CH_3 and back to reactants C3CC. + O_2 become very competitive with stabilization channel while the rate of stabilization decreases. Also the rate of isomerization to C3.CCOOH decreases a little with increasing temperature. This is because the A factor becomes dominant rate controller. For the same reason, direct dissociation to C3CCO. + O from chemically activated C3CCOO.* will have the largest increase of the reaction rate with increasing temperature. At 700 K, a fraction (approximately 10 % at 1.0 atm) of the chemically activated C3CCOO.* directly reacts to products via the isomerization to C3.CCOOH channel. This is responsible for formation of C2CyCCOC, one of major products. The other isomerization channel to C3CC.OOH has a low rate at 700 K while the channel of C3CC.OOH to product C3CCHO + OH has a very high rate (E_a is only ca. 2.5 kcal-mol^{-1}), so almost all energized C3CC.OOH* adduct goes to product with almost no reverse reaction. The chemical activation channel C3CC. + O_2 → C3CCHO + OH also contributes to OH formation.

Figure IC. 1(b) illustrates the pressure dependence for the rate constants of the chemically activated reactions. In the pressure range from 0.1 to 100 atm, the channels of

stabilization, dissociation back to reactants, isomerization to C3.CCOOH and its dissociation products have much higher rates than other channels. Stabilization to C3CCOO. is the dominant product channel over almost all pressures. The back to reactants channel will be dominant when pressure is lower than 0.1 atm. The stabilization and isomerization to C3.CCOOH have almost the same increasing rate below atmospheric pressures while isomerization decreases when pressure increases to above atmospheric pressure. Other product channels decrease too relative to stabilization as the pressure increases.

4.3.2 Chemical Activation Reaction System: C3.CCOOH + O_2 → Products

The second O_2 addition to neopentyl hydroperoxide radical is important at low temperature and high O_2 concentration conditions and it is responsible for the production of acetone [50,64],a second major product from neopentyl radical oxidation.

The energy level diagram and input parameters for addition of a second O_2 to hydroperoxide isomer and subsequent reactions are shown in Appendix ID. 2. The reaction channels for C2C(COOH)COO.$^{\bullet}$ radical are similar to C3CCOO.$^{\bullet}$, reverse reaction, isomerization and stabilization. Two isomers result from intramolecualar hydrogen transfer, and are important in this second O_2 addition. C2.C(COOH)COOH will eliminate a C.H_2OOH to form hydroperoxide olefin (C=C(C)COOH) and the C.H_2OOH rapidly undergoes elimination (exothermic) to CH_2O + OH. This isomer can also form an epoxide + OH as in the first O_2 addition. C2C(COOH)C.OOH will rapidly eliminate OH to form hydroperoxide carbonyl (C2C(COOH)C=O). Both the hydroperoxide carbonyl and olefin will undergo dissociation, cleavage of the weak O-O bond in the peroxy moiety with

products OH and alkoxy, serving to accelerate the oxidation (chain branching reaction). These alkoxy radicals are important sources to form 2-methyl-2-propenal (C=C(C)CHO) which was identified as an important products from oxidation of neopentyl radical [50]. The sensitivity analysis shows that this second O_2 addition reaction pathway also contributes to the OH formation.

The apparent rates of chemical activation channels from C3.CCOOH + O_2 to various products shows a similar tendency to the first O_2 addition C3CC. + O_2 (Figure IC. 1.

4.3.3 Chemical Activation Reaction System: C2C=C + OH, O_2 → Products

The OH addition to iso-butene, followed by O_2 addition to intermediate radical, is the key reaction pathway to account for secondary product formation. OH can add to each side of carbon double bond in iso-butene to from two intermediate radicals C3.COH and C2C.COH. Temperature and pressure dependence of these two addition reactions are in Appendix Figure IC. 1 and Figure IC. 1, which show they are pressure dependent reactions at the temperature above 700 K and are negative temperature dependent reactions in the all pressure range. The C3.COH and C2C.COH radicals will quickly react with O_2 with no barrier to form chemically activated, energized adduct $[C2C(OH)COO.]^*$ and $[C2C(OO.)COH]^*$, which then undergo stabilization, isomerization and further beta scission, or dissociation back to reactant. The QRRK analysis (Appendix Figure IC. 1 and Figure IC. 1 shows that the adducts will most go back to reactant at temperature above 700 K, pressure below 1 atm. With the decreasing temperature and increasing pressure, stabilization becomes dominant channel and certain fraction of adduct can directly go to product C2C=O and CH_2O (from dissociation of $C.H_2OOH$)

4.3.4 Fate of Stabilized Peroxy and Hydroperoxide Adducts

The computed results for the rate of O_2 addition to neopentyl radical as well as other O_2 additional chemical activation pathways above show that the main product path of chemically activated adducts is stabilization for almost all pressures and at intermediate or above temperatures. It is, therefore, important to determine the fate of the stabilized peroxy and hydroperoxide adduct as a function of temperature. QRRK analysis results for these stabilized adducts and some of their products are shown in Appendix Figure IC. 1.

4.3.4.1 C3CCOO. and C3.CCOOH

C3CCOO. peroxy radical and C3.CCOOH hydroperoxide radical are from major reaction pathway C3CC. + O_2 and are responsible for the major product C2CyCCOC formation. Our results (Appendix Figure IC. 1 show that at atmospheric pressure, the dominant reaction of stabilized C3CCOO. is dissociation to C3CC. + O_2 when temperature is above 900 K; is isomerization via a H atom shift followed by a beta scission to a cyclic ether + OH when temperature is below 700 K. This account for the formation of C2CyCCOC, while major product channel of stabilized C3.CCOOH is C2C=C + C.H_2OOH, which account for a part of C2C=C formation.

4.3.4.2 C2C(COOH)COO., C2.C(COOH)COOH, C2C(COOH)C.OOH

The dominant path for stabilized C2C(COOH)COO. radical is dissociation back to C3.CCOOH + O_2. The dominant product channel from this peroxy radical is C=C(C)COOH + C.H2OOH (these can further form C=C(C)CHO, CH_2O). Two hydroperoxide radicals C2.C(COOH)COOH and C2C(COOH)C.OOH are intermediates resulting from isomerization of stabilized C2C(COOH)COO. radical or directly from

chemically activated adduct [C2C(COOH)COO.]* (C3.CCOOH + O_2). They both can go back or go further as beta scission reactions. QRRK analysis (Appendix Figure IC. 1) shows that the C2.C(COOH)COOH will mainly undergo reverse reaction with a small fraction undergoing beta scission to C=C(C)COOH + C.H_2OOH, while the product channel of C2C(COOH)CHO + OH from C2C(COOH)C.OOH is dominant over the temperature range because of very low or no barrier for this type beta scission with carbonyl formation. The secondary product C=C(C)CHO. is from these pathways.

4.3.4.3 C2C(OH)COO., C2C(O.)COOH, C2C(OOH)CO., C2C(OO.)COH

These four stabilized adducts C2C(OH)COO., C2C(O.)COOH, C2C(OOH.)CO. and C2C(OO.)COH are from OH / O_2 addition to iso-butene. The QRRK analysis (Appendix Figure IC. 1) show that the C2C(OH)COO. and C2C(OO.)COH will mostly go back to reactants and have certain fractions to product C2C=O + C.H_2OOH (from C2C(OH)COO.) and C2C.OOH + CH_2O (from C2C(OO.)COH) in the temperate range of 500 to 1300 K, and isomerization to C2C(O.)COOH, C2C(OOH.)CO. will be dominant at temperature below 500 K. The C2C(O.)COOH, C2C(OOH.)CO. will go to product C2C=O + C.H_2OOH, C2C.OOH + CH_2O separately at temperature above 700 K and go back to their isomers at temperature below 700 K.

4.3.5 Unimolecular Dissociation Reaction Systems

The most important unimolecular dissociation reaction in neopentyl radical + O_2 system is neopentyl radical dissociation to iso-butene and methyl radical. The QRRK analysis (Appendix Figure IC. 1) show that it is pressure dependent reaction at temperature above 700 K. This reaction will be discussed in more detail in the following chapter.

4.3.6 Summary

The QRRK analysis have showed that the two primary major products: (1) 3,3-dimethyloxetan (DMO, C2CyCCOC) (2) iso-butene (C2C=C) from the oxidation of neopentyl radical under the molecular oxygen atmosphere and at intermediate temperature were produced by chemically activated reaction pathway of C3CC. + O_2 via the neopentyl hydroperoxide isomer C3.CCOOH, and unimolecular dissociation of neopentyl radical.

The OH formation will be accounted by product channel of the first O_2 addition to neopentyl radical. C2CyCCOC + OH, C3CCHO + OH, as well as the second O_2 addition to neopentyl hydroperoxide isomer.

The reactions C3CC. → C2C=C + CH_3 and C3.CCOOH → C=C(C)COOH + CH_3 are responsible for the formation of methane (CH_4), and the reaction C3.CCOOH → C2C=C + C.H_2OOH may account for the formation of formaldehyde (CH_2O) because all C.H_2OOH rapidly undergoes dissociation with a ca. 2.5 kcal-mol^{-1} activation energy to form CH_2O.

The QRRK analysis also shows that the dominant product channel of a chemically activated adduct above 0.1 atm and below 900 K is, stabilization, because isomerization has a relative low A factor (tight transition state). Fall off at 700 K occurs because of adduct dissociation (reverse reaction). The important isomer (C3.CCOOH) product channel is C2CyCCOC + OH, and next important product channels are C2C=C + C.H_2OOH and C=C(C)COOH + .CH_3. Subsequent reactions of this stabilized isomer with O_2 will also be important at conditions where stabilization occurs and O_2 is present. The

channel to C3CC=O + OH (endothermic, beta scission of the C3CC.OOH) also has some significance.

CHAPTER 5

MODELLING VALIDATION FOR THE NEO-C_5H_{11} + O_2 SYSTEM

5.1 Basic Model of Neopentyl + O_2 System

The model contains 58 reactions and 39 species and the mechanism is listed in Table IA. 4 It has been shown to describe set of experimental data well; but it is significantly different in description of the neopentyl + O_2 reaction from that of Hughes et al [54], and of Baldwin and Walker [50]. It also comparable to literature data for important reactions. We conclude an isomerization barrier height some 7 kcal $mole^{-1}$ lower than that of the above two research groups and that subsequent barriers are responsible for the apparent barrier reported by Hughes et al. We also show that while one reaction is responsible for a major fraction of the OH formation - (more than half), the total OH is actual by the result of several reaction paths. The importance of these paths will change with varied conditions (oxygen concentration, pressure and temperature). And we show that reactions of the hydroperoxy-neopentyl radical with oxygen can have significant contributions to the OH profile.

5.2 Validation by Hughes' Data

Hughes et al [54] conducted a direct measurements of the neopentyl peroxy-hydroperoxide radical isomerization over the temperature range 660 - 750 K in 1992. They obtained their results by monitoring the OH profile. In this work we have attempted to model set of their experimental result and thus validate our mechanism.

The Senkin [71] computer code from Sandia is used to integrate the kinetic equations and calculate reverse rate constants from the forward rate constants and thermodynamic parameters. A comparison of the time dependence of the OH radical formation to data published by Hughes et al is illustrated in Figure IC. 20 and a comparison of the energy of activation vs. temperature to the experiment results of Hughes is shown in Figure IC. 21. The results for OH profile and the temperature dependence of rate constants show very good agreement with experimental data of Hughes et al 54]. Sensitivity analysis on OH profile at the mean experimental temperature indicates that the A factor for the formation of C2CyCCOC and the well depth (Enthalpy of neopentyl peroxy) of the adduct are important. The most important reactions for the OH profile are C3CC. radical reaction with O_2 (chemical activation) and unimolecular decomposition.

Table IA. 3 shows that there are several reactions responsible for the OH formation. The OH radical is generated by three major paths: (i) Dissociation of hydroperoxy alkyl isomer to OH + a cyclic ether and others (Appendix ID. 1); (ii) The addition of a second O_2 to hydroperoxy alkyl radical with isomerization and subsequent reaction of the isomer (Appendix ID. 2); (iii) Methyl radical oxidation and subsequent reactions. Table IA. 3 shows that at pressure near 1 atm and 700 K, the formation of epoxide is the most important channel to form OH radical. The addition of O_2 to C3.COH and C2C.COH with isomerization and subsequent reaction of the isomers (Appendix ID. 5, ID. 6) does not show an importance to the OH profile; but our analysis shows that C3.COH and C2C.COH are important intermediates in this reaction system. These species are produced by addition of OH radical to iso-butene, a major initial product from neopentyl radical decomposition and some from the neopentyl radical + O_2 reaction paths. These

hydroxyl adducts undergo addition reaction with O_2, isomerization (hydrogen transfer of the OH hydrogen to the peroxy group) and unimolecular decomposition of the alkoxy radical to an alkyl-C.H_2OOH, which rapidly undergoes exothermic reaction to a ketone or aldehyde + OH (Appendix ID. 5, ID. 6). The hydrogen shift in these isomers is facilitated via hydrogen bonding between the peroxy oxygen radical and the OH group and may be responsible for an important and stable product, acetone, formation in neopentyl oxidation.

Some important reaction fluxes are listed in Table IA. 5. The data shows that addition of O_2 to alkyl radicals are in near equilibrium and the epoxide formation is faster than other dissociation paths excluding reverse isomerization of the hydroperoxy radical by a factor of 10.

5.3 Validation and Comparison with Literature Data for Important Reactions

5.3.1 Comparison with Slagle's Data for C3CC. → C2C=C + CH_3 (k_1)

Our QRRK analysis is shown to describe Slagle et al's experimental data [49] well for neopentyl radical decomposition reaction.

The unimolecular dissociation of neopentyl radical has been widely investigated with the studies of the pyrolysis of neopentane. Furimsky and Laidler [48] investigated this reaction as a special part of the whole study for neopentane pyrolysis and reported the first set of experimentally based high pressure limit rate constant, 2.5×10^{13}exp(-29.001 kcal-mol^{-1}/RT) s^{-1}, by extrapolating their experimental data obtained at the temperature of 529 to 608 K and pressure of 0.0355 to 0.296 atm with neo-C_5H_{12} as bath gas. This rate has

been considered too high because they assigned a too high A factor for the reference reaction they used for derived absolute rate constant. A two set of rate constants of 2.0×10^{13}exp(-29.8 kcal-mol^{-1}/RT) s^{-1} (in 1975), 2.51×10^{13}exp(-29.637 kcal-mol^{-1}/RT) s^{-1} (in 1979), for unimolecular dissociation of neopentyl radical to iso-butene and methyl radical were derived, by Szirovicza and Marta [72], from fitting a complex mechanism of neopentane pyrolysis under the temperature range from 512 to 571 K, and pressure range from 0.0158 to 0.259 atm. Muller et al [73] reported a rate constant of 1.00×10^{13}exp(-30.00 kcal-mol^{-1}/RT) s^{-1} derived from fitting a complex mechanism while they investigated the influences of HCl and HBr on the pyrolysis of neopentane and ethane at small extents of reaction. More recently, Baldwin et al [50] calculated a rate of $10^{13.65\pm0.2}$exp(-30.474 kcal-mol^{-1}/RT) s^{-1} for their neopentane oxidation mechanism in 1982 while Tsang [74] derived a rate of 1.07×10^{13}exp(-29.808 kcal-mol^{-1}/RT) s^{-1} from detailed balance and reverse rate in 1985. The latest report for neopentyl radical decomposition is $10^{13.9}$exp(-31.5 kcal-mol^{-1}/RT) s^{-1} by Mitchell and Benson [51] when they reinvestigated the apparent discrepancy between previous reports.

Only one particular study on unimolecular decomposition of the neopentyl radical is conducted by Slagle et al [49]. They directly monitored the decomposition of neopentyl radical by using a heatable tubular reactor coupled to a photoionization mass spectrometer. Their experimental temperature and pressure were 560 - 650 K and 0.00132 - 0.0118 atm.

The rate of $10^{13.9}$exp(-30.76 kcal-mol^{-1}/RT) s^{-1} in this study derived from fitting a simple mechanism for oxidation of neopentyl radical in the O_2 atmosphere and quite comparable

to other studies (Table IA. 2). A comparison of our QRRK calculation result to the experimental data reported Slagle et al [49] is made and shown in Figure IC. 19 A very good agreement between our QRRK calculation under their experimental condition and their experiment data is obvious while the rate becomes lower when we directly took their high pressure limit rate constant for our QRRK analysis.

5.3.2 Fall-Off Analysis for C3CC. + O_2 → C3CCOO. ($k_2/k_{-2}=K_2$)

The reaction of O_2 addition to neopentyl radical was studied only by Bayes group [52, 53] at a very low pressure of 3 Torr and they found high pressure rate constant, $\{2.1\times10^{12}$ cm^3-$molecule^{-1}$-$s^{-1}\}(T/300\ K)^{-(2.1\pm0.4)}$ for C3CC. + O_2, a negative temperature dependence (rate constant decrease with increase temperature), k ranged from 1.7×10^{12} cm^3-mol^{-1}-sec^{-1} at 266 K to 6.91×10^{11} cm^3-mol^{-1}-sec^{-1} at 374 K. The rate constants used by Hughes et al [54] and Curran et al [64] and this study are originally referenced to Bayes et al experimental study on this particular reaction but in different way. We took the average k reported by Bayes et al, using 1.0×10^{12} cm^3-$mole^{-1}$-sec^{-1} as the high pressure limit k_∞ for our QRRK analysis while Hughes et al and Curran et al directly extrapolated Bayes' low pressure and low temperature data for their modeling studies without fall-off considerations. Baldwin et al [50] used Benson's additivity data with an assumed internal rotational energy barrier of 10 kJ-mol-1 for the t-C_4H_9 group to get an equilibrium constant of $2.7\times10^{-5}\exp(+105.1\ kJ\text{-}mol^{-1}\ /\ RT)\ dm^3\text{-}mol^{-1}$.

A full fall-off analysis is illustrated in Figure IC. 18. Figure IC. 18 (a) shows a negative temperature dependence of the rate of reaction C3CC. + O_2 → C3CCOO. and this dependence goes smaller when pressure goes higher. Figure IC. 18 (b) shows that almost

no fall-off at 300 K but the rates go down with decreasing pressures more rapidly at higher temperatures. above 700 K. At 300 K, we calculated only 1.8% fall off from the high pressure limit using 1.0×10^{12} cm^3-$mole^{-1}$-sec^{-1} to 3.0 Torr. If one extrapolates the low pressure data of Bayes' to 700 K, $k_{(C3CC. - O2)}$ is 2.13×10^{11} cm^3-$mole^{-1}$-sec^{-1}; to 753 K, $k_{(C3CC. - O2)}$ is 1.83×10^{11} cm^3-$mole^{-1}$-sec^{-1}. Hughes et al [54], whose experiment are at 550 Torr, 700 K and Curran et al [64], who modeled the experimental data reported by Baker et al [61, 62] at 500 Torr,753 K, both used this low k (2.13×10^{11} cm^3-$mole^{-1}$-sec^{-1} and 1.83×10^{11} cm^3-$mole^{-1}$-sec^{-1}) in their modeling. At 700 K, we calculated a 90.9% decrease in k due to fall off at 3 Torr, 38.9% at 550 Torr from the average high pressure limit k ($k_{\infty(avg.)}$, 1×10^{12} cm^3-$mole^{-1}$) so there is about 50% increase in k from 3 Torr to 550 Torr at 700 K due to fall-off. At 753 K, we calculated a 95.7% fall off at 3 Torr, 57.5% at 500 Torr from high pressure limit k (k_∞) so 35% difference between 3 Torr and 500 Torr at 753 K. So a direct (temperature only) extrapolation of Bayes' low pressure data to 700 K or 753 K for higher pressure experiment is not justified. Our QRRK analysis yields an $A_{700\ K}$ of 4.54×10^{11} at 550 Torr and 4.75×10^{11} at 1 atm with A_∞ as estimated 1.0×10^{12} cm^3 $mole^{-1}$ sec^{-1}.

The flux of this reactions is calculated and shown in Table IA. 5, which shows that reaction_C3CC. + O_2 ⇔ C3CCOO. is effectively at equilibrium in the modeling (conditions: 700 K, 550 Torr) with forward rate of 1.02×10^{-9} cm^3 $mole^{-1}$ sec^{-1} and reverse rate of 1.07×10^{-9} cm^3 $mole^{-1}$ sec^{-1} at 1.0 millisecond, and forward rate of 3.67×10^{-10} cm^3 $mole^{-1}$ sec^{-1} and reverse rate of 3.82×10^{-10} cm^3 $mole^{-1}$ sec^{-1} at 1.8 millisecond. The kinetic aspect of this reaction is well controlled by the thermodynamic properties. A sensitivity

analysis on our mechanism has also been performed by varying A_∞ from 1.0×10^{12} cm^3 $mole^{-1}$ sec^{-1} to 6.0×10^{12} cm^3 $mole^{-1}$ sec^{-1}, and found the results shown in Figure IC. 21, which shows only small differences.

5.3.3 MOPAC Calculation for C3CCOO.→ C3.CCOOH

There were no specialized study except Hughes et al [54] focused on this isomerization reaction, a intramolecular H transfer via a 6 member ring transition state. The different sets of A factor and activation energy for this isomerization reaction are listed in Table IA. 2 Transition State theory incorporated semi-empirical calculation method MOPAC PM3 is used in this study to describe this H transfer reaction (see section 1.3 MOPAC) and we calculated an A factor of $10^{9.77}T^{0.71}$ and activation energy of 22.7 kcal-mol^{-1} as high pressure limit rate constants for QRRK analysis.

Hughes et al [54] obtained an A_∞ factor of 1.585×10^{12} and $E_{a,\infty}$ of 29.4 kcal-mol^{-1} derived from experimentally determined rate constants versus temperature. Their result was based on their assumption that only one reaction C3.CCOOH → C2CyCCOC + OH responsible for the formation of OH and the isomerization is the rate-determining step, so they monitor OH profile and plot time constants obtained from bi-exponential fits to the OH profile versus O_2 concentration, then obtained their experimentally determined rate constants by fitted into this curve with assigned rate constants for k_1 (C3CC. → C2C=C + CH_3), K_2 (C3CC. + O_2 → C3CCOO.) (see section "5.3.1 Comparison with Slagle's Data for C3CC. → C2C=C + CH3" and "5.3.2 Fall-Off Analysis for C3CC. + O2 → C3CCOO.").

Baldwin et al [50] obtained rate of $10^{13.08}$exp(-28.7 kcal-mol^{-1} /RT) from their experimental determined value of $k_2k_3/k_{-2}k_1$ ($A_2A_3/A_{-2}A_1$ and $E_{a2}E_{a3}/E_{a-2}E_{a1}$) with their calculated k_1 and K_2. The $k_2k_3/k_{-2}k_1$ values were determined by applying stationary-state treatment to the equation d([acetone]+[DMO]) / d[iso-butene] = $K_2k_3[O_2]/k_1$ and found the initial product yield ratio R = ([acetone] + [DMO]) / [iso-butene] by extrapolating experimental determinations. Their result was based on their proposed simple mechanism: iso-butene is accounted by neopentyl radical dissociation, DMO is accounted by neopentyl hydroperoxide radical dissociation and acetone is from a second O_2 addition to neopentyl hydroperoxide isomer.

Curran et al [63] calculated a rate of $10^{12.35}$exp(-23.9 kcal-mol^{-1} /RT) by using transition state theory but without MOPAC calculations for A factor.

5.3.4 Rate Constant for C3.CCOOH → C2CyCCOC + OH (k_4)

Table IA. 2 lists set of Arrhenius parameters for this epoxide formation reaction. This is a somewhat faster reaction and account for most of OH formation. Baldwin et al calculated a rate constant of $10^{11.30}$exp(-17.46 kcal-mol^{-1} /RT) based on their experimental determined value for k_4/k_6 (k_6 is the rate of reaction C3.CCOOH → C2C=C + CH_2O + OH, see following discussion). Curran et al get their self-consistent rate of $10^{10.40}$exp(-15.25 kcal-mol^{-1} /RT) based on their previous on the formation of oxetan species from an alkyl hydroperoxide radical. We calculated an A factor of $10^{7.76}$ using MOPAC PM3(see section 1.3 MOPAC) and obtain a n of 0.71 and E_a of 14.0 kcal-mol^{-1} by best fitting Hughes experimental results.

5.3.5 Beta Scission Reaction C3.CCOOH → C2C=C + C.H_2OOH

The sensitivity analysis in our mechanism shows that the β-scission of C3 CCOOH to C2C=C + C.H_2OOH is account for a part of iso-butene. The rate of this reaction is also important in the explanation of products distribution. Baldwin et al took the same A factor as one they calculated for neopentyl radical dissociation but lower about 12 kJ-mol^{-1} for activation energy for consideration of the presence of less effective OOH group Curran et al and this study calculated the rate constants based on reverse reaction and considered a methyl likened radical C.H_2OOH addition to the double bond in iso-butene. Curran et al directly took rate constant of the reverse reaction of neopentyl dissociation from Slagle [49]. We took the same E_a as methyl addition to ethylene and lower A factor to $10^{11.2}$ from $10^{11.5}$.

5.4 Conclusion for Neo-C_5H_{11} + O_2 System

We have evaluated thermodynamic properties, reaction paths and kinetic parameters for the neopentyl radical + oxygen reaction system and the sub-system of neopentyl peroxy isomer: neopentyl hydroperoxide radical + O_2 reaction system as well as neopentyl unimolecular decomposition reaction and further iso-butene reaction system. Quantum RRK theory is used to calculate k(E) with the modified strong collision of Gilbert et al used to calculate fall off effects in a kinetic analysis on the chemical activation reaction systems. The rate constants are incorporated into a detailed, elementary reaction mechanism, which is used to model the set of experimental results.

Enthalpies of reactants, intermediates, products and transition states for the elementary reactions resulting from addition of neopentyl radical to molecular oxygen are evaluated in

this study and are illustrated in Appendix IA, Appendix IB. Potential energy diagrams are constructed for QRRK analysis, and high pressure rate constants are taken from evaluated literature data or estimated as described above, they are illustrated in Appendix ID.

The temperature and pressure dependencies of reactions are calculated with QRRK analysis and are illustrated in Appendix IC.

We also defined transition states for two important reactions — isomerization of neopentyl peroxy radical to neopentyl hydroperoxide radical and the formation of cyclic ether from neopentyl hydroperoxide isomer (C3.CCOOH) and calculate pre-exponential A factors from transition state theory. All information for these two transition states are summarized in Appendix IB. We calculate transition state structures and evaluate barriers to isomerization and epoxide formation reactions as 22.7 and 14.0 kcal $mole^{-1}$ respectively. Flux analysis indicates that a number of these peroxy dissociation and isomerization reactions are at or near equilibrium. Thermodynamic equilibrium and bleed reactions such as: slow epoxide + OH formation relative to reverse isomerization, addition of a second O_2 to the neopentyl hydroperoxide primary alkyl radical, isomerization and subsequent dissociation of this second peroxy, serve to control oxidation rate in this 700 K, 550 Torr reaction system.

PART III

FUNDAMENTAL STUDY ON MTBE PYROLYSIS AND OXIDATION

CHAPTER 6

INTRODUCTION

6.1 Overview

MTBE, Chemically named 2-methoxy-2-methyl-propane or methyl tert-butyl ether ($C_5H_{12}O$), CAS NO. 1634-04-4, is a combustible, but relatively stable (in storage), clear and colorless liquid of low viscosity. It has a distinct odor that is responsed to be neither pleasant nor nauseating. It's other chemical/physical properties are MW = 88.15; MP = -109 °C; BP = 55.2 °C; d = 0.7404 $g\text{-}ml^{-1}$ (20/4 °C) and VP (vapor pressure) = 245 mmHg at; RVP (Reid Vapor Pressure) = 4.7 psi at 25 °C.

As it is more commonly known, MTBE is a motor fuel oxygenate and octane enhancer. It has been a preferred choice of petroleum industry as an octane enhancer in gasoline since 1980's because it seems to be an efficient way [75] to meet the emission control and fuel composition requirements of the 1990 Clean Air Act with no additional capital investment to change the additive main manufacture route. It is currently being blended with gasoline up to 15 volume percent and the amount may be raised up to 30 volume percent according to legislation and regulations under the Clean Air Act Amendments (CAAA) of 1990. MTBE is accepted as oxygenate in the reformulated gasoline and oxygenated gasoline by US Environmental Protection Agency (EPA), to improve and ameliorate the air quality of the ozone non-attainment areas and carbon monoxide non-attainment areas, because it allows the gasoline to burn more cleanly [76] in the engine and significantly reduces exhaust emissions (CO and hydrocarbon) [77].

The effect of MTBE blending on the properties of gasoline has been reviewed by Mamid et al [78]. MTBE effectively boosts the octane number of gasoline without adversely affecting its other properties, and it provides a much higher FEON, (Front End Octane Number) which becomes more important in cold start conditions and characterizes the efficiency of the engine, to the gasoline pool. It is not affected by the lead (Pb) concentrations in the gasoline so it can readyly make up the lost of octane number due to elimination of lead in the gasoline. MTBE has favorable effect on the vapor pressure and distillation characteristics of the gasoline because it has lower RVP (Reid Vapor Pressure) relative to other octane enhancers such as butane. MTBE addition lowers the distillation temperature, which improves driveability, carburation, and cold engine operation. MTBE-gasoline blend are free of gums and peroxides after long term storage and it is more stable during handling and storage than alcohols. It has a good water tolerance and poses no phase separation problems, blending in just like a hydrocarbon in distribution systems and in the presence of water. MTBE appears to be the most economical way to increase octane number while accomplishing environmentally desirable goals, and enhancing octane rating.

MTBE's chemical, physical and thermal properties, are compatible with that of gasoline, especially in the boiling range where gasoline typically shows the lowest antiknock characteristics, this makes it one of the fastest growing chemicals in the world and by far the largest-volume oxygenate used in US. The rapidly increasing demand for MTBE is also due to the lower production cost related to that of alcohol and the lead-phase down regulations of the CAAA of 1990.

Many practical benefits are shown from related studies done on MTBE-gasolines. However, concerns and questions about its environmental and health effects [79 - 81] arose, in recent years, from scientists, researchers, occupational workers and consumers. The environmental concerns focus on the products and by-products after combustion of MTBE and reactions in atmosphere after evaporation from motor fuel distribution, storage and fueling operations plus products after combustion.

MTBE is an effective octane booster and volume extender for unleaded gasoline, but it is not as efficient as tetra-alkyl lead compounds, whose antiknock characteristics had been identified by [82] as a chain breaking mechanism (chain termination), as far as specific octane number improvements are concerned. The improvement of blending properties by the addition of MTBE has been evaluated to depend not only on characteristics of the base gasoline (composition of gasoline which contains hundreds of components in different concentrations) but also on the relative concentration of MTBE.

New questions arise such as: How does MTBE behavior change in gasoline, so as to become an octane enhancer? Does it produce toxic by-products? How MTBE-gasoline will affect the environment can be evaluated from the actural elementary chemical process, what is the reaction mechanism and the product distribution of MTBE oxidation under the real or near typically combustion conditions in the internal combustion chamber. The fundamental combustion chemistry of oxygenated hydrocarbons (OHC's) such as MTBE is becoming more and more important as federal, state and community as well as individuals become more concerned about the environment in which they live. Answering to these questions are becoming more urgent as the EPA continues to propose more restrictive regulations or mandates on petroleum industry.

The more scientists and researchers understand the fundamentals of why MTBE has good anti-knocking properties, the better refiners and engineers can control the combustion and improve engine design to obtain more clean burning in the internal combustion chamber

Development of a fundamentally based, pressure dependent, reaction mechanism for MTBE to use in modeling combustion and low temperature oxidation is becoming more important and necessary because the combustion of hydrocarbon and OHC's in practical devices such as internal combustion engines occurs at pressure well above atmospheric conditions, i.e. pressures up to 40 atm.

6.2 Objective of this Study

The goals of this part study are :

- Development and advancement of the understanding of oxidation and pyrolysis processes on MTBE under high pressure conditions.
- Identification of important reactions and key species in the high temperature chemistry of MTBE.
- Identify product distributions of MTBE oxidation and pyrolysis under the experimental conditions by acquisition of experimental data from lab experiments on oxidation and pyrolysis of methyl tert-butyl ether (MTBE).
- Development of a pressure and temperature dependent elementary kinetic model for MTBE, based on thermochemical kinetic principles, tested against experimental data. This will allow computer experiments to suggest trends for future experimental testing

and preferred fuel compositions that can lead to reduced hydrocarbon emissions while hopefully maintaining or improving engine performance.

A fundamentally based, and pressure and temperature dependent elementary reaction model is targeted to describe both literature and experimental data from this lab for MTBE in the combustion and low temperature oxidation regimes. This includes detailed reaction paths for the major products and for the second major products. A pressure dependent analysis is performed by QRRK calculation coupled with beta collision analysis for fall-off effects on unimolecular decomposition and isomerization reaction and on bimolecular chemical activation reactions [83]., for rate constants under the experimental pressure (1 to 10 atm) conditions. The concentration of reactants, intermediates and final products predicted by the mechanism are coupled (tested) against experimental data. Particular importance is directed to reactions of primary radical intermediates with O_2, such as C3C. + O_2, C2.C=C + O_2 and C=CC. + O_2, plus HO_2 and OH addition reactions with iso-butene, which is a major product of MTBE pyrolysis and oxidation and then subsequent reactions of these radical adducts with O_2. A second importance is directed to the reactions of methanol, an other major product from MTBE pyrolysis and oxidation.

The experiments are conduced in tubular flow reactors to obtain reactant loss and intermediate species profiles versus reaction time, pressure and temperature for pathway analysis and model validation.

6.3 Literature Review

There are a number of studies on 1 atm oxidation and pyrolysis of MTBE for the overall reaction reactants, stable products, as well as some studies on total rate of OH abstraction.

A more limited number of health effect studies have been reported [81]. There are no published studies, however, on a detailed reaction mechanism that focus on both pressure and temperature effects of initial reactions of MTBE coupled with detailed analysis of primary and secondary products from the initial processes. A fundamental study on high temperature chemistry of MTBE is necessary to understand important aspects of fuel combustion in internal engine combustion chamber such as emission or knock.

6.3.1 MTBE Pyrolysis

Early studies on thermal pyrolysis of MTBE were all conducted at temperature below 800 K and all concluded that MTBE decomposes nearly exclusively through the formation of a four-center transition state, followed by the decomposition to iso-butene and methanol.

Daly and Wentrup [84] reported that the thermal decomposition of MTBE produced iso-butene and methanol with no iso-butane formation and with unimolecular rate constant of $10^{14.38}\exp(-61.54\ \text{kcal-mol}^{-1}/RT)\ s^{-1}$ over the temperature range from 706 to 768 K. The fact that added excess iso-butylene did not change the rate of iso-butene production led them first to suggest that four-center transition states for the decomposition of MTBE and lock of any radical intermediates.

Choo et al [85] conducted thermal decomposition of MTBE in a VLPP (Very Low-Pressure Pyrolysis) reactor coupled with a quadrupole residual gas analyzer for product and reactant identification. They confirmed a four-center transition state mechanism for MTBE decomposition to iso-butene and methanol by their experimental conduction and RRKM calculations. They recommend a value of $10^{13.9}\exp((-59.0\pm1.0\ \text{kcal-mol}^{-1})/RT)\ s^{-1}$ over the temperature range from 888 to 1158 K.

One study on pyrolysis of MTBE was done by Brocard and Baronnet [86]. MTBE was decomposed thermally in a static or low flow reactor over the temperature range from 623 to 763 K at the low pressures of 0.0658 to 0.197 atm. They used gas chromatography to analyze products and reactants and reported an absolute rate constant value of $10^{14.0}\exp(-59.6\ \text{kcal-mol}^{-1}/RT)\ s^{-1}$ for reaction C3COC → C2C=C + CH_3OH. They also concluded a four-center unimolecular elimination path accounts for the homogenous thermal decomposition of MTBE over the temperature and pressure range of their study.

A summary of these pyrolysis data (rate constant for C3COC → C2C=C + CH_3OH) includes:

Dalvand Wentrup [84]	$k = 10^{14.38}\exp(-61.54\ \text{kcal-mol}^{-1}/RT)\ s^{-1}$
	$E_a - \Delta H_{rxn} = 46.35\ \text{kcal-mol}^{-1}$
	$k_{600} = 9.0 \times 10^{-9}$; $k_{800} = 3.69 \times 10^{-3}$; $k_{1000} = 8.50 \times 10^{0}\ (s^{-1})$
Choo [85]	$k = 10^{13.9}\exp((-59.0 \pm 1.0\ \text{kcal-mol}^{-1})/RT)\ s^{-1}$
	$E_a - \Delta H_{rxn} = 43.18\ \text{kcal-mol}^{-1}$
	$k_{600} = 2.5 \times 10^{-8}$; $k_{800} = 6.03 \times 10^{-3}$; $k_{1000} = 1.01 \times 10^{1}\ (s^{-1})$
Brocard and Baronnet [86]	$k = 10^{14.0}\exp(-59.6\ \text{kcal-mol}^{-1}/RT)\ s^{-1}$
	$E_a - \Delta H_{rxn} = 44.41\ \text{kcal-mol}^{-1}$
	$k_{600} = 1.9 \times 10^{-8}$; $k_{800} = 5.21 \times 10^{-3}$; $k_{1000} = 9.40 \times 10^{0}\ (s^{-1})$
Average	$k = 10^{14.03}\exp(-60.05\ \text{kcal-mol}^{-1}/RT)\ s^{-1}$
	$E_a - \Delta H_{rxn} = 44.65\ \text{kcal-mol}^{-1}$
	$k_{600} = 1.77 \times 10^{-8}$; $k_{800} = 4.98 \times 10^{-3}$; $k_{1000} = 9.33 \times 10^{0}\ (s^{-1})$

6.3.2 Abstraction Reactions of MTBE by OH Radical

The abstraction reaction of Hydrogen atom from MTBE by OH radical, serves an important role in the oxidation of MTBE process at intermediate temperatures, and has been widely studies since MTBE was introduced in large quantities as an gasoline additive to increase the octane and reduce CO emissions in the late 1980's.

Cox and Goldstone [87] measured the total abstraction rate constant of reaction from MTBE by OH radical using the relative rate technique at temperature of 295 K and 1 atm pressure. Their experiments were conducted in a static reaction system with gas chromatography to examine the products and reactants. They reported rate ratio of 0.44 relative to a reference reaction between OH radical and n-hexane and obtained a normalized overall value of 1.51×10^{-12} cm^3-$molecule^{-1}s^{-1}$.

Wallington et al [88] conducted a flash photolysis resonance fluorescence study on the kinetics of the reaction of OH radical with MTBE and reported an overall value of rate constant as $k = (5.1\pm1.6)\times10^{-12}\exp[(-(155\pm100)/T]$ cm^3-$molecule^{-1}s^{-1}$ over the temperature range 240 - 440 K at total pressure between 25 to 50 Torr. This rate constant includes abstractions from both the methyl ether hydrogen and the primary methyl tert-butyl hydrogen by OH radical. They produced OH radicals, at an intial concerntration estimated as $10^{10} \le [OH]_0 \le 10^{11}$ molecules-cm^3, by the vacuum ultraviolet ($\lambda \ge 165$ nm) photolysis of H_2O ($\approx$ 0.1 Torr). They monitored OH radicals as a function of time under pseudo-first-order kinetic conditions by fluorescence at 300 nm excited by a microwave OH resonance lamp. Reaction was in Pyrex reaction cell and the reactant mixture flowed through the reaction vessel to avoid the accumulation of photolysis or reaction products. The initial concentration of MTBE, $(0.5\text{-}4.0) \times 10^{14}$ molecules-cm^3 was high enough to assure pseudo-first-order kinetic conditions with respect to the radical decay.

Wallmington et al [89] investigated the abstraction reaction between OH radical and MTBE again but under different conditions by relative rate measurement method. The OH radicals were formed through the photolysis of methyl nitrite (CH_3ONO) in reactant

mixture, a synthetic air consisting a reference organic (n-butene or diethylether), MTBE and CH_3ONO, at atmospheric pressure (about 740 Torr). Analysis was carried out on a gas chromatograph equipped with a split/splitless injector and FID and fitted with either a 30 m × 0.25 mm (film thickness 0.25 μm) DB-5 column or a 30 m × 0.53 mm GS-Q column. They used 10 to 20 ppm as typically initial concentrations for both the reference and reactants and 50-100 ppm concentration for methylnitrite. They reported a consistent overall value of (3.24±0.08) × 10^{-12} cm^3-$molecule^{-1}s^{-1}$ with their previous value [88]. We note again that these experimants present only the overall rate not on analysis of the tert-butyl versus methoxy C---H hydrogen.

6.3.3 MTBE Oxidation

In 1991, Tuazon et al [90] first focused on the product investigation from the OH radical-initiated oxidation of MTBE under atmospheric (lower troposphere) conditions. They reported the major products are t-butyl formate (TBF), formaldehyde (CH_2O), methyl acetate ($CH_3C(=O)OCH_3$), acetone ($CH_3C(=O)CH_3$), acetaldehyde (CH_3CHO), peroxyacetyl nitrate ($CH3C(=O)OONO_2$, PAN) and NO2 in the presence of NO_x, products were identified by on-line Fourier transform infrared absorption spectroscopy and/or on batch gas chromatography.

Smith et al [91] investigated the OH radical-initiated oxidation of MTBE, with methyl nitrite as the source of OH radical by a photolysis technique. They reported a product distribution consistent with Tuazon [90]. An overall value of (2.99±0.12) × 10^{-12} cm^3-$molecule^{-1}s^{-1}$ at 298 K for abstraction reaction between OH radical and MTBE with n-butane as a reference is reported.

Dunphy and Simmie's[92] reported on oxidation of MTBE conducted in reflected shock waves over a temperature range from 1024 to 1850 K and a pressure of 3.5 bar in an argon diluent. The reactant mixture composition varied widely, with equivalence ratios varying from 0.25 for a fuel-lean, 1.0 for a stoichiometric, to 2.5 for a fuel-rich mix. Measurements of the ignition delay times, characterized by chemiluminescence and pressure increase, led them to conclude that high temperature oxidation of MTBE is, in essence, that of methanol and iso-butene production for stoichiometric and fuel-rich mixtures, but is not for fuel-lean mixture. The probable reason is that the rate of oxidation of MTBE at high concentration of O_2 is much faster than the rate of MTBE via only reaction C3COC $\rightarrow$ C2C=C + CH_3OH, and then the faster rate of oxidation of methanol + iso-butene.

Norton and Dryer [93] presented experimental results for flow reactor oxidation of MTBE at equivalence ratio 0.96, initial temperature of 1024 K and atmospheric pressure. Gas samples extracted at fifteen positions along the reactor duct centerline were quenched in the hot-water-cooled probe and stored at 343 K for subsequent gas chromatographic analysis. The purity of the MTBE was only 97%. The main products they observed are iso-butene and methanol. At 1024 K, 50% MTBE is converted in a time of about 5 msec, and 90% of conversion is achieved at about 40 msec. Iso-butene and methanol are generated at up to 75% and 40% of initial MTBE concentration, and decay slowly compared to the MTBE decomposition rate. At 1024 K and residence times to 100 msec, increased amounts of carbon monoxide, acetone, propyne and C5 are produced with increased MTBE conversion. Methane and propene are observed at about 10% of MTBE initial concentration. Other observed, low concentration, products (less than 10% of

MTBE initial concentration) are C_2H_2, C_2H_4, C_2H_6 and CO_2. Norton and Dryer describe the result of MTBE decay by the unimolecular elimination reaction only, which occurs through a four-center activated complex.

An experimental and kinetic modeling study on oxidation of MTBE was recently reported by Held, Dryer et al [94] again using the Princeton atmospheric pressure flow reactor (\PFR), the same apparatus as that used by Norton and Dryer [93], but at two temperatures of 1028 K and 1119 K, and at equivalence ratios near one. The concentrations of the hydrocarbon intermediates, plus CO and CO_2 were determined by gas chromatograph with SP-1000 and Porapak Q and R packed columns, FID and TCD detectors. They found significant quantities of acetone in the intermediates and again larger quantities of iso-butene than methanol. A detailed chemical mechanism was developed to describe their experimental results. They explained acetone production by considering the MTBE decomposition reactions other than four-center elimination: specially by cleavage of the methyl-ether C-O bond to form $(CH_3)_3O$. radical and then invoke this oxy radical's decomposition to form acetone. The non-unity ratio of iso-butene and methanol was accounted for by the abstraction reactions of methyl-ether hydrogen in MTBE to form $(CH_3)_3OCH_2$ radical followed by formaldehyde elimination from this radical to produce excess iso-butene without formation of methanol. This abstraction pathway accounts for approximately 10-15% of the fuel consumption for the low temperature conditions and 5-10% for the 1119 K experiment.

CHAPTER 7

EXPERIMENTAL STUDY ON MTBE PYROLYSIS AND OXIDAITON

7.1 Experimental Conditions

Pyrolysis and oxidation of MTBE under high pressure conditions (4 to 10 atm) are conducted over the temperature range 798 to 1123 K at four equivalence ratios. The temperature range represents MTBE conversion from 0 to 100 percent in a 6 second time regime. The pressures are 4, 7 and 10 atm. Residence times range from 0.3 to 6 seconds and are limited by the required flow rate for ensuring needed amount of MTBE entering the reactor. Three reaction ratios for oxidation of MTBE represent fuel lean, stoichiometric and fuel rich. Pyrolysis of MTBE, the fourth, is carried out in the same way by varying temperature, pressure and residence time. The specific experimental conditions are listed in Appendix Table IIA. 1.

7.2 Experimental Apparatus

Reactions of MTBE in argon bath gas are carried out in a high pressure reactor which is a heavy wall (6 mm) quartz tube with 6 mm ID, housed in 75 cm length of three zone Chemshell 1.25" ID electric tube furnace equipped with three independent Omega Model CN-310 digital temperature controllers. A Neon Controls BPS 26G2501, 200 psi back pressure regulator is used to maintain the desired pressure within the reactor.

A diagram of the experimental apparatus is shown in Appendix Figure IIC. 1. Reactant MTBE is HPLC grade supplied by Fisher Co. Methane, argon and helium gases are reagent grade supplied by Liquid Carbonic Co. and filtered (activated carbon and

molecular sieve) of O_2, H_2O, and hydrocarbon impurities before entering the reactor system.

7.3 Flow Control and Measurement

The carrier gas (argon) is passed through 273 K saturator for feed of vapor MTBE. Sufficient contact time is achieved, by increasing the length of the saturation column, to insure saturation of MTBE in the Argon carrier. A second argon stream is used as additional make-up gas to control the desired mole fraction between reagents. Methane and oxygen were brought into the flow stream as required. The flow rate for each gas is controlled by Union Carbide LINDE Model FM-4550 mass flowmeter-flowcontroller with individual mass flow control module which is well calibrated before experiment. The calibration curves of mass flow controllers are in Appendix Figure IIC. 2 - Figure IIC. 4.

The reactants (feed mixture) are mixed in about 20 cm of the flow tube located upstream of the furnace and preheated to about 373 K to prevent condensation and to improve reactor temperature control. The reactants can either flow through the reactor or flow directly to a GC sampling valve via a bypass line. The bypass is used to determine the initial concentration of reactants without going through the high temperature reactor. All gas lines to the analytical equipment are held at 373 ± 10 °K to limit condensation. A fraction (5%) of the outlet gases from the reactor is passed to the analytical device through a Tee connector while the bulk of the effluent flows through a sodium bicarbonate ($NaHCO_3$) flask for neutralization before being released to the atmosphere via exhaust into a fume hood.

Gas samples are drawn through a separate sampling line by means of a mechanical vacuum pump, from the reacted flow to fume hood, with a constant flow rate of 45 cm^3 min^{-1}. An HP-5890 Series II gas chromatograph with two flame ionization detectors (FID) is used on-line for analysis.

7.4 Temperature Control and Measurement

Temperature profiles are obtained at each flow using a shielded type K thermocouple probe moved axially within the 75 cm length reactor with a representative flow of inert. Thermocouple error caused by furnace wall radiation is minimized by using a sheath. The darkened outside surface of the quartz tube reactor also served as a second radiation shield. Heater control resulted in temperature profiles isothermal to within ± 5 K over 80 - 85% of the furnace length for each temperature. Temperature gradients of 500 K in 5 cm at the inlet and outlet of the reactor occur. Uncertainty in absolute temperature measurements is estimated to be ± 1% (i.e. ± 8-12 K) but relative temperatures are measured to within ± 5 K. The temperature profiles are shown in Appendix Figure IIC. 5 and Figure IIC. 6 with and without reactions present.

7.5 Qualitative and Quantitative Analysis

The reaction time was measured as: $t = V / F_{T,P} = \pi (D/2)^2 L_{eff.} / F_{T,P}$, where V is the effective volume of reactor, $F_{T,P}$ is flow rate (cm^3 / sec) at reactor temperature and pressure, D is the diameter of reactor in cm, $L_{eff.}$ is effective length of the constant high temperature zone of the reactor in cm. $L_{eff.}$ is obtained from temperature profiles. $F_{T,P}$ is calculated from flow rate at room temperature and atmospheric pressure ($F_{298K,1atm}$), which

is controlled by mass flowmeter. A small computer code was used to calculate the flow of each reagent for the desired residence times at each temperature and pressure.

An HP-5890 Series II gas chromatograph with two flame ionization detectors is used on-line to determine the concentrations of reactants and products. A ten-port VALCO gas sampling valve is employed to introduce the gas samples into the GC columns. Gas samples are passed through two sampling loops, 1.0 cm^3 and 0.25 cm^3, at a constant flow rate of 45 cm^3 per minute, and then injected into a packed column and a capillary column, respectively.

Two columns, one packed and one capillary, are used to perform separations of the hydrocarbond, oxy-hydrocarbons and CO + CO_2. The 6' × 1/8" feet stainless steel column packed with 50% 80/100 Poropak T and 50% 80/100 Poropak Q is used for the separation of CO, CO_2 and light hydrocarbons. A catalytic converter containing 5% of 80/100 ruthenium on alumna catalyst with constant flow (about 24.4 cc / min) of H_2, connected in series after the packed column and held at about 300 C°, is used to convert the CO and CO_2 to methane after GC column separation therefore CO and CO_2 can be quantitative analyzed by FID. A 90 m × 0.53 mm Hewlett Packard fused silica capillary column is used for heavier hydrocarbon and oxy-hydrocarbon separation. The chromatogram peaks are analyzed with two HP 3396A integrators. The carrier flow was about 24 cc / min for packed column and 9 cc / min for capillary column.

Calibration to obtaining appropriate molar response factors and retention times of relevant compounds is performed by injecting known concentrations of standard gases and known

quantities of liquid samples. The average retention times and relative response factors are shown in Appendix Tables IIA. 2.

Product identifications are also verified by HP 5899A GC/Mass Spectrometry, with a HP 90 m × 0.53 mm fused silica capillary, on batch samples of reactor gas drawn from the reactor exit into evacuated 25 cm^3 stainless steel sample cylinders for later analysis.

7.6 Experimental Results

7.6.1 MTBE Oxidation

7.6.1.1 Fuel Lean Environment

Experimental results of 0.5% MTBE pyrolysis and oxidation under three pressures and selected temperatures are presented in Appendix IIC Figure IIC. 7 to Figure IIC. 16.

Fuel lean P = 4 atm:

Figure IIC. 7 - Figure IIC. 10 present the results of oxidation of MTBE in the fuel lean (phi = 0.75) environment, a pressure of 4 atm, and three temperatures of 823, 873 and 923 K.

70-80% of MTBE decays in about 1.0 second at 823 K. Significant amount of C2C=C, CH_3OH (1 - 6 × 10^{-3} mole fraction), CH_2O, C_3H_6 (1 - 2 × 10^{-4} mole fraction), and some C2C=O, and C=C(C)CHO (1 - 5 × 10^{-5} mole fraction), are produced. A steadily increasing amount of CO is observed, at low level (less than 2 × 10^{-4} mole fraction) with increased MTBE conversion. No CH_4 or CO_2 is observed at this temperature. When temperature increase to 873 K, over 80 % of the MTBE is converted to products with

similar product distribution in the same time scale of 0.6 - 1.2 sec. Both C2C=C, and CH_3OH have a lower concentration level at 873 K than that at 823 K and reach a peak at 0.85 sec. The level of formaldehyde (CH_2O) appears constant (stable) in this temperature range of 823 to 873 K, while C_2H_4, C_3H_6, C2C=O and C=C(C)CHO increase with time but show no change with time at 823 K. Results at 823 K and at 873 K suggest that the further oxidation of major products C2C=C and CH_3OH start as early as at 873 K in the fuel lean mixture (equivalence ratio = 0.75) and result in formation of products C_2H_4, C_3H_6, C2C=O and C=C(C)CHO but not significant quatities of CH_2O. At 923 K, all intermediate products presented in the 823 and 873 K conditions are converted to final product CO_2 at about 0.6 second, the only detected product at this temperature is CO_2.

Fuel lean P = 7 atm:

Figure IIC. 11 - Figure IIC. 13 present oxidation of MTBE, φ = 0.75, at pressures of 7 atm and residence time to 4.0 sec. At about 1.0 sec, the conversion of MTBE is lower than 40% at 798 K, over 40% at 823 K and 100% at 873 K. Higher concentration of major products C2C=C and CH_3OH are produced when temperature increases from 798 to 823 at about 1.0 sec. None of C2C=C or CH_3OH, two major products are observed at 873 K, CO_2 is the only detected product. At 4 atm, the concentration of both C2C=C and CH_3OH start to decrease at 873 K (as at 4 atm) and they completely convert to final product at 923 K in less than 0.2 sec. The increased pressure is observed to speed oxidation of C2C=C and CH_3OH as well as the overall rate of MTBE decay to final product CO_2 Increasing the pressure will lower the temperature for complete conversion of MTBE.

Fuel lean P = 10 atm:

Figure IIC. 14 - Figure IIC. 16 show the results at 10 atm. MTBE is completely converted to CO_2 at 823 K. Comparing results at 10 atm to those at 7 atm at 798 K (Figure IIC. 11) and residence time about 1.6 sec, the highest peak or concentration points of C2C=C, CH_3OH, CH_2O and C_3H_6 are about 1.6 sec at 10 atm, and 2.6 sec at 7 atm; Increasing pressure speeds the overall reaction rate.

Higher level of C2C=C related to CH_3OH are produced from fuel lean mixtures as is observed in all pressures and temperatures. For these fuel lean conditions, at 4 atm, complete loss of MTBE occurs at 898 K, 0.65 sec, complete conversion of MTBE and major products occurs at 923 K, in less than 0.4 sec; at 7 atm, complete conversion of MTBE and major products occurs at 873 K and in less than 0.8 sec; at 10 atm, complete loss of MTBE occurs at 823 K, 1.60 sec, complete conversion of MTBE and major products occurs at 873 K and in less than 1.6 sec.

7.6.1.2 Stoichiometric Environment

Figure IIC. 17 - Figure IIC. 36 in Appendix IIC show MTBE oxidation results at stoichiometric environments and three pressures of 4 (residence time 0.4 to 1.2), 7 (residence time 0.8 to 3.4), and 10 atm (residence time 1.2 to 5.6 seconds).

Stoichiometric P = 4 atm:

Product distributions over temperature range from 823 to 1073 K at 4 atm are presented in Figure IIC. 17 to Figure IIC. 23. Conversion of MTBE at 0.7 sec is about 40% at 823 K, 70% at 873 K, and 100% at the temperatures of 923 K or above. When temperature increases from 823 to 873 K, the amount of major products C2C=C and CH_3OH increase

30% for 0.8 sec residence time. They reach a maximuma concentration point at 0 85 sec at 873 K. At 823 K the concentration level of major products continue to increase with residence time and did not yet reach a maxim at 1.2 sec. CH_2O, C_3H_6, C2C=O and C=C(C)CHO as well as C_2H_4, C_2H_2, and C_2H_6 all have higher concentration levels at 873 K than that at 823 K in the same residence time range. The concentration level of all these products increase with residence time and have not yet reach a maxima in observed time range. A faster increase of CO with time accompanies the MTBE conversion at 873 K.

A different product distribution is found when temperature is increased to 923 K from 873 K. We note the difference in Figure IIC. 20 to Figure IIC. 19. Higher concentrations of CO and much higher levels of CO_2, and CH_4 along with much lower levels of major products are observed at 923 K. The second observation is that much more C_2H_4 (100 times at 0.55 sec) and more C2C=O (2 times at 0.5 sec), C_2H_2 (100 times at 0.5 - 0.6 sec),, and C_2H_6 (100 times at 0.5 - 0.6 sec), are produced. C2C=C and CH_3OH are at much lower level (100 times at 0.6 sec),, CH_2O levels remain similar at 873 K and 923 K. A third observation is that all product levels start to decrease with time at 923 K. The forth observation is that C2C=C and CH_3OH are now approximately equal in level. Figure IIC. 21 (973 K) and Figure IIC. 23 (1073 K) show that at increased temperature, an increase of CO_2 level occurs with a continue decrease in level of all products are observed at 973 K, and a complete conversion to CO_2 with some CO of all products at 1073 K is observed. An important change is the new ratio of C2C=C to CH_3OH at 973 K. The ratio of C2C=C to CH_3OH is larger than 1 below 923 K, almost equal to 1 at 923 K, and less than 1 at 973 K.

A summary for stoichiometric oxidation of MTBE at 4 atm, with reactant MTBE decay, major products C2C=C and CH_3OH produced first increase, then decrease with residence time, the levels of these two products increase from 0.4 to 1.2 sec, below 873 K, reach a maxima at 0.8 sec and start to decrease at 873 K, and undergoes rapidly decay above 873 K, complete convertion to CO_2 occurs at 1073 K in less than 0.5 sec.. Oxidation of the major products C2C=C and CH_3OH, lead to C_2H_4, C2C=O, C_2H_2, C_2H_6, this indicates that the oxidation of C2C=C and CH_3OH is one of the major sources responsible for these products.

Comparing fuel lean oxidation of MTBE at 4 atm and 0.7 to 1.0 sec, to stoichiometric oxidation, 70% of conversion of MTBE occurs at 823 K for fuel lean environment, only 40% at 823 K for stoichiometric; 70% conversion occurs at 873 K for stoichiometric. Complete conversion to CO_2 from MTBE occurs at 923 K (fuel lean) and 1073 K (stoichiometric) respectively. This indicates that increased O_2 (more fuel lean) increases the overall rate of MTBE decay. Higher concentrations of major products C2C=C, and CH_3OH are observed in stoichiometric than that in fuel lean environment (Figure IIC. 8 and Figure IIC. 19). This indicates that high $[O_2]$ results in faster oxidation of major products. In both fuel lean and stoichiometric environments maximum concentration levels of C2C=C and CH_3OH occur at 873 K indicates that temperature (798 to 1073 K) does not affect the point on time frame for relative levels of the major product distribution, this is also seen from other product distributions.

Stoichiometric P = 7 atm:

Figure IIC. 24 -29 present the experimental results at the pressure of 7 atm and at 798 K, 823 K, 873K, 923 K, 1023 K and 1073 K respectively. Conversion of MTBE is about

40% at about 1.0 sec at 798 K, 50% at 823 K, almost 100% at 873 K (100% conversion does not occurs until 923 K at 4 atm). The maximum concentration levels of C2C=C, CH_3OH and CH_2O (7 atm, φ = 1) are located at 823 K, and at 873 K for 4 atm in both fuel lean and stoichiometric environments). Maxima of C2C=O, C_3H_6, C_2H_4 are at 873 K in this 7 atm case. Figure IIC. 26 shows that C2C=C is lower than CH_3OH at this 873 K temperature. This reverse of the ratio of C2C=C to CH_3OH at 4 atm occurs at 973 K. Complete oxidation of CH_3OH at 7 atm occurs at 1073 K in less than 0.8 sec (Figure IIC. 29).

Stoichiometric P = 10 atm:

Results at 10 atm are shown Figure IIC. 30 to Figure IIC. 36. Similar product distributions are observed to data at 4 and 7 atm, with maximum levels of products observed at lower temperature at 798 K.

One difference between the data at 7 atm versus 10 atm in this stoichiometric environment is that and small HC's such as CH_4, C_2H_4, C_2H_6, C_2H_2 appear more stable at higher temperatures and pressures.

7.6.1.3 Fuel Rich Environment

Reducing the O_2 level in the reactant fuel mixtures decreases reactant decay and different trends of product distribution occur as shown in Figure IIC. 37 - 61.

At 4 atm and about 1.0 sec, MTBE conversion is near 50% at 823 K, 85% at 873 K, and complete at 898 K in 0.7 sec. At 823 K (Figure IIC. 37), observed products are C2C=C, CH_3OH and CH_2O, C_3H_6 with C2C=C and CH_3OH at higher levels than CH_2O, C_3H_6 (50 - 100 times at 0.6 sec). At 873 Figure IIC. 39, C2C=C and CH_3OH reach a maxima at

0.75 sec and start to decrease with residence time. CH_2O, C_3H_6, C2C=O and C=CC(C)CHO as well as C_2H_4 increase with time in 0.5 - 1.2 sec but C_2H_4 is 100 times lower than CH_2O. At 923 K (Figure IIC. 41, CO is high with little CO_2 and CH_4 observed. All other product levels start to decrease with increased residence time (0.5 - 1.2 sec) except C_2H_4 remains at the same level. The ratio of C2C=O to CH_3OH becomes less than 1 at 973 K. Continuing increase of temperature to 1048 K from 998 K. CO increases about 10%, CO_2 increase by 50%, and CH_4 remain unchanged in 0.5 - 1.2 sec. No C2C=C was observed at 1048 K, 0.5 - 1.2 sec, CH_3OH is much lower in concentration (mole fraction less than 3×10^{-6}), the major product in addition to CO, CH_4 and CO_2 now is C_2H_4 and C_2H_2, C_2H_6, CH_2O are at higher concentration levels than CH_3OH and C_3H_6 (ca 10 times). C2C=C and C2C=O as well as C=C(C)CHO are not observed at this 1048 K, 4 atm and fuel rich environment.

Affects of pressure increase to 7 atm and 10 atm, at 1.0 sec, MTBE conversion is about 10% at 798 K and quickly goes to 100% at 823 K at 7 atm; 20% at 798 K and 100% at 823 K at 10 atm. Figure IIC. 44 - 61 show that CO increases quickly with residence time and temperature, and reaches a maxima at 898 K (mole fraction 0.021) at both 7 atm and 10 atm while the maximum concentration level of CO at 4 atm is observed at 1048 K (mole fraction 0.017). A larger overall rate is shown under the higher pressure conditions, which is similar to that in other two oxidation environments (φ = 0.75, 1.0). The reverse of the ratio of C2C=C to CH_3OH, from, greater than 1, to, less than 1, occurs with increase temperatures, 973 K at 7 atm; 998 K at 10 atm.

Comparing to other two oxidation environments (φ = 0.75, 1.0) which have higher [O_2] in the reactant fuel mixtures, the obvious change is that the levels of CO_2 increase with [O_2] as shown as following data (in mole fractions):

	4 atm (0.4 - 1.2 sec)	7 atm (0.8 - 3.4 sec)	10 atm (1.2 - 5.6 sec)
φ = 1.5	0.0025 at T = 1048 K	0.003 at T = 1048 K	0.003 at T = 1048 K
φ = 1.0	0.02 at T = 1023 K	0.01 at T = 923 K	0.01 at T = 873 K
φ = 0.75	> 0.025 at T = 923 K	> 0.025 at T = 873 K	> 0.025 at T = 823 K

CO and CH_4 show higher concentrations than in fuel lean and stoichiometric environments. C_2H_4, C_2H_2, and C_2H_6 become dominant products under the higher pressures and fuel rich environment. Major products C2C=C and CH_3OH further react faster when O_2 is present. This affects the concentration levels of both C2C=C and CH_3OH in relative higher temperatures (φ = 0.75: > 873 K at 4 atm; > 798 K at both 7 atm and 10 atm. φ = 1.0: > 873 K at 4 atm; > 798 K at both 7 atm and 10 atm. φ = 1.5: > 873 K at 4 atm; > 823 K at 7 atm and > 798 K at 10 atm). The ratio of C2C=C to CH_3OH also changes with decreased temperature, pressure and oxygen level in fuel mixture. Pressure change affects the overall rate and product distribution, but not temperature dependence of the relative product ratio.

7.6.2 MTBE Pyrolysis

Experimental results on MTBE pyrolysis over temperature range from 823 to 1123 K at 4 atm, 7 atm, and 10 atm are presented. The distribution of major and important products profiles is illustrated in Appendix Figure IIC. 62 - 85.. These figures show that under the experimental conditions of pyrolysis: (1) C2C=C and CH_3OH are unique major products up to temperature at 1123 (4 atm), 1048 K (7 atm), 998 K (10 atm); (2) CH_4 is a much

more important product than CO and CO_2 and is at a high concentration level at high temperatures; and (3) Differences between C2C=C and CH_3OH are smaller compared to those in the three oxidation environments; and (4) less CH_2O, C2C=O and C=C(C)CHO are observed from pyrolysis, which indicates that much of these carbonyl species are from oxidation paths of reactant and major products.

7.6.2.1 At the Pressure of 4 Atm, Pyrolysis

Figure IIC. 62 -69 present the pyrolysis results of MTBE at 4 atm over temperature of 823 K to 1123 K. At 1.0 sec, MTBE decay is about 30% at 823 K, 55% at 873 K, 80% at 923 K and complete loss at 973 K in 0.9 sec. At 823 K, C2C=C and CH_3OH are major products with only two minor products CH_2O and C_3H_6 at very low concentration (1000 times lower). At 873 K, the MTBE conversion is higher and C2C=C and CH_3OH increase 15% in 0.5 - 1.1 sec, mole fraction of CH_2O increases to 9×10^{-6} at 873 K from 3×10^{-6} at 823 K at 0.8 sec, mole fraction of C_3H_6 increases to 3×10^{-6} at 873 K from 5×10^{-7} at 823 K at 0.8 sec, and C2C=O is observed at $1\text{ -}2 \times 10^{-6}$ (mole fraction, in 0.5 - 1.0 sec) as the third minor. When temperature continues to increase to 923 K, the levels of three minor products C2C=O, CH_2O and C_3H_6 increase by about 8 - 12 times in 0.5 - 1.0 sec, while major products C2C=C and CH_3OH increase by only 5%. C2C=O increases faster than all others and CH_2O increases slower than C2C=O and C_3H_6, which may due to the greater stability of C2C=O than CH_2O at higher temperatures. At 973 K, all products continue to increase with four more products CH_4, C_2H_4, C_2H_6 and C_2H_2 observed in very low concentration levels. The latter three are new members in minor products group and there is a large difference between the higher levels of C2C=O, C_3H_6, CH_2O and lower

levels of these new species (C_2H_4, C_2H_6, C_2H_2). At 1023 K, CH_4 has a higher concentration level (0.004 - 0.009 in mole fraction in 0.4 - 1.0 sec) and all other products remain almost the same level as that at 973 K except C_3H_6, C_2H_4, C_2H_6 and C_2H_2 increases by 2 - 5 times in 10 sec. Increasing the temperature to 1048 K from 1023 K, C2C=C (0.0014 mole fraction) and CH_3OH (0.00117 mole fraction) remain unchanged in 0.5 - 1.1 sec. Changes are observed in minor product distribution, CH_4 has significant increase (mole fraction is 0.0016 at 1048 K and 0.0008 at 1023 K, at 0.8 sec) and start to compete with C2C=C and CH_3OH. Little difference is now observed between the other members of the minor products group, C_3H_6 has the highest level and C_2H_4, C_2H_6, C_2H_2 increase by about 0.5 - 1.5 time in 0.5 sec. At 1073 K, CH_4 continues to increase and is similar to C2C=C and CH_3O, which start to decrease with the residence time (0.5 -1.0 sec.), C2C=O decreases with the time and CH_2O reaches a maxima at 0.7 sec then start to decrease with the time. Further increasing temperature to 1123 K, show all products except C2C=O and C=C(C)CHO are competing (similar in concerntration) with CH_4, all products decrease with the residence time (0.5 - 1.1 sec).

7.6.2.2 At the Pressure of 7 Atm, Pyrolysis

Experimental results at 7 atm are presented in Appendix Figure IIC. 70 - 77. Conversion of MTBE, at 1 sec, is about 25% at 873 K, 75% at 923 K, 100% at 973 K. Major products are C2C=C and CH_3OH, and minor products are C_3H_6, C2C=O and CH_2O at 873 K. C_2H_4 is observed at 923 K in very low concentration (1.1×10^{-6} mole fraction). CH_4, C_2H_2 and C_2H_6 are observed at 973 K. All products increase with the increasing temperature (873 K to 923 K to 973 K), C2C=O and C_3H_6 increase faster than the others.

At 998 K and 1023 K (Figure IIC. 73 - 74), major products C2C=C, CH_3OH and two minor products C2C=O, CH_2O decrease with residence time (0.6 - 3.0 sec), while small HC's CH_4, C_2H_4 and C_3H_6 still increase with residence time. When temperature increases to 1048 K (Figure IIC. 75), CH_4 start to compete with major products and rapidly increase with the residence time (0.6 - 3.0 sec), CO is observed to increase with time. At 1123 K, experiment show that CH_4 decrease and CO increase with residence time (0.6 - 3.0 sec); C2C=C rapidly decreases with residence time; CH_3OH, C_3H_6 decrease with residence time and their concentration are higher than that of C2C=C. C_2H_4 does not change with the time.

7.6.2.3 At the Pressure of 10 Atm, Pyrolysis

Figure IIC. 78 - 85 are experimental results at 10 atm under the conditions of pyrolysis. MTBE conversion at 1.0 sec, is about 20% at 873 K, 60% at 923 K, 100% at 973 K. The product distribution profiles observed at 10 atm are very similar to that at 7 atm with faster overall reaction rate.

Comparison of pyrolysis results at the three pressures, at the same temperature, we can see that with the higher pressure, MTBE decay becomes slower (not much); products have a little bit higher concentrations (in the unit of mole fraction); overall reaction rates are faster. Pressure change does not affect product distribution profiles nearly as much as in case of oxidation but does affect concentration levels a little.

7.6.3 Temperature and Pressure Dependence of Product Distributions

Temperature and pressure dependence of important product decay are showed in Appendix Figure IIC. 86 - 124. The discussion above has illustrated temperature and pressure dependence of important product profiles. Increasing temperature always change product distribution profiles. This change becomes more complicated in oxidation environments and is smoother in pyrolysis case. Temperatures always bring faster decay of reactant MTBE, and speeds oxidation of products when O_2 is present. Pressure seems to shift product distribution profiles versus residence time but does not change temperature dependence of product distribution profiles. In the pyrolysis environment, pressure has less effect on overall reaction than that in oxidation environments.

MTBE decay in the presence of O_2 becomes faster at about 873 K and is complete at 923 K in fuel lean environment. The more O_2, the shorter time needed for MTBE complete oxidation in three pressures. The pyrolysis of MTBE shows very similar temperature decay curves at three pressures. Not like oxidation in which case there seems be a certain temperature point at which oxidation becomes very rapid. Pyrolysis shows a smooth change with temperature.

7.6.4 Conclusion

Experimental data were collected at 4, 7, 10 atm, temperatures of 798 K to 1123 K, and 0.4 sec to 1.2 sec (4 atm), to 3.8 sec (7 atm), to 5.6 sec (10 atm). The major products from both oxidation and pyrolysis of MTBE are iso-butene and methanol, with acetone and formaldehyde as important minor species at relative low temperatures. Small hydrocarbons, C_3H_6, C_2H_4, CH_4, are present along with C2C=C and CH3OH or dominate

at low [O_2] and high temperature conditions. CO_2 is produced with more O_2 in reactant fuel mixture and there is no CO_2 observed in pyrolysis environment. Little CH_4 is produced in fuel lean environment and high levels (0.008 in mole fraction) are observed in pyrolysis environment. CO is observed in all environments and its concentration level is dependent on [O_2] and temperatures. Important secondary products are C2C=O, CH_2O, CH_4, C_2H_4, C_3H_6, C2CyCOC, C=C(C)CHO, C2C=C=O, C=C(C)COH, C2CCOH, CO and CO_2. More iso-butene than methanol is produced under the conditions of high O_2 levels and relative lower temperatures, the ratio of C2C=C to CH_3OH changes from, greater than 1, to near 1, to less than 1 with increased temperature. The difference between the amount of this two major products becomes small in pyrolysis environment compared to oxidation. Experimental data also show MTBE decay is much faster as expected in high O_2 concentration (more fuel lean) mixtures than pyrolysis environments and product distributions are more complex in oxidation than pyrolysis. Formaldehyde and iso-butene are more dominant in the low temperatures in the pyrolysis situation. MTBE conversion increases with increased temperature at constant pressure and stoichiometry; increases with decreased stoichiometry (more fuel lean) at constant temperature and pressure; increases with increased pressure at constant temperature and stoichiometry.

CHAPTER 8

MODELLING STUDY ON MTBE PYROLYSIS AND OXIDATION

8.1 Overview

What is the reaction mechanism and product distribution of MTBE decay under the real or near typically combustion conditions and how the pressures affect the mechanism become a valuable research topic after many experiments conducted by several research groups. Only a few research groups provide kinetic information for this system as we discussed in chapter 6. One of the goal of this study is to build a detailed, pressure and temperature dependent, kinetic mechanism for MTBE pyrolysis and oxidation. Specific emphasis has been placed on understanding and properly treat using the pressure dependent reactions and identifying important reactions and key species in the high temperature chemistry so the model can be applied to both atmospheric and internal engine oxidation / combustion.

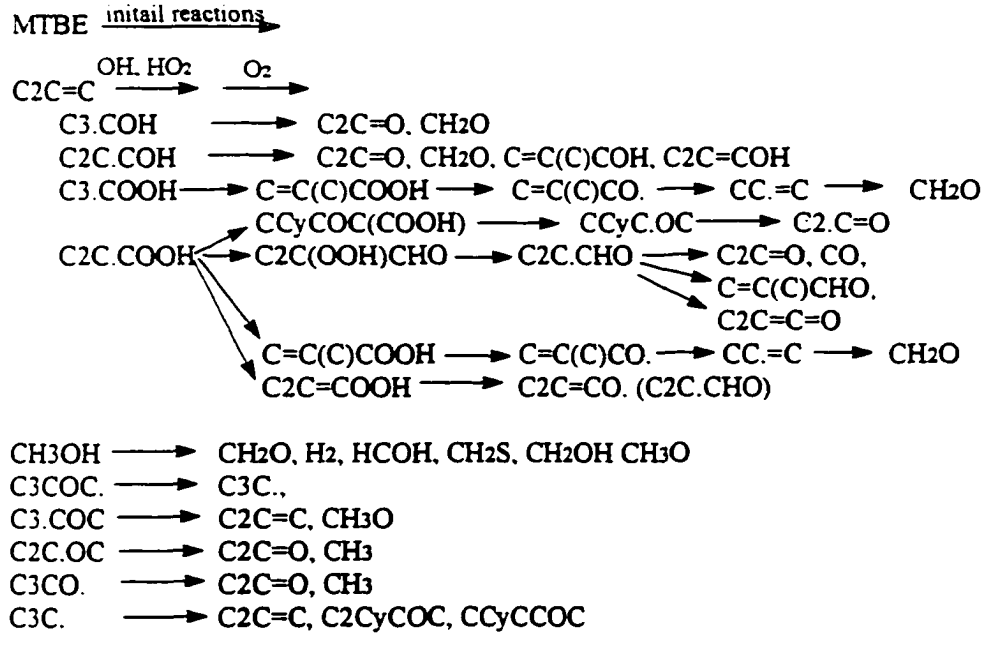
In this study, we consider the dissociation and abstraction by O_2 as the initial reactions of MTBE oxidation. Specific abstraction reactions between MTBE and OH, H, O, HO_2, CH_3 are also considered in the initial reaction part.

MTBE decomposites at lower temperatures, up to 1000 K, primarily by molecular elimination reaction, to products iso-butene + methanol. Iso-butene has six allylic type carbon - hydrogen bonds, bond energy ca 88 kcal-mol^{-1}, which are readily attached by primary, secondary, and tertiary alkyl radicals as well as by H, O, OH radicals, all of which have stronger C---H bond energies, so the abstraction reactions are exothermic.

R. + C2C=C $\rightarrow$ C2.C=C + energy

The weak C---H bonds in iso-butene serves to capture the more active radicals, noted above, and produce the relatively non-reactive allylic iso-butenyl radicals. Reactions of allylic like radicals with O_2, for example, form an adduct which has a very shallow well, only 18.5 kcal-mol^{-1}, and the dominant adduct reaction is reverse to the allylic radical and O_2.

The initial radicals from MTBE dissociation reactions are C3C., C3CO., C3COC., C3.COC, and C2C.OC, which all have further reactions to stable products or other radicals. The important product formation pathways are illustrated as follows.



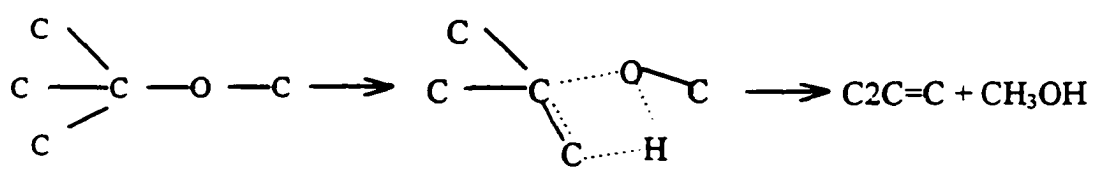
8.2 Methods for Kinetic Modeling Study

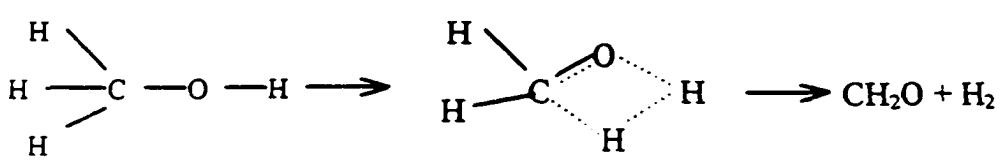
Thermodynamic parameters ΔH_{f298}, S_{298} and $C_p(300)$ to $C_p(\text{infinity})$ for all species involved in the modeling mechanism are listed in Table IIA 1. The calculation methods and rules obtaining these thermodynamic properties are described in chapter 1. The principle of

obtaining and/or estimations of input parameters for QRRK calculations are also described in chapter 2. One extra ordinary feature here, however, is that QRRK calculations with beta collision for fall off incorporate not only temperature but also pressure dependence (0.001 to 100 atm, 200 to 2500 K) into rate constant expressions by employing Chebyshev polynomials (7 × 3). A modified Chemkin Interpreter is used to incorporate the combined pressure and temperature dependent rate expression into the Senkin or Chemkin integrators [83].

8.3 Important Transition States

The semi-empirical calculation method MOPAC PM3 is used to find the transition states thus rate constants (A factor) for many important reactions including isomerization reaction, elimination reactions and β-scission reactions in this modeling study. Most of transition state structures and their thermodynamic properties are directly taken from reference [95] or calculated by Bozzelli's research group in NJIT. Transition states for MTBE dissociation to C2C=C + CH_3OH and CH_3OH to CH_2O + H_2 are calculated in this study and listed in Appendix IIB along with the information for the transition states related to MTBE, C2C=C and CH_3OH reaction.





The transition states for MTBE and CH_3OH dissociation will be discussed in the following section. The transition states for the important C2C=C related reactions are listed in here and detailed in Appendix IIB.

	ID	Reactions
TS 1	TC2C*JCXH	C3C. → C2C=C + H
TS 2	TC2YCQC	C3COO. → C3.COOH
TS 3	TC2YCXQC*	C3COO. → C2C=C + HO_2
TS 4	TC3*CXQ	C3.COOH → C=C(C)OOH + CH_3
TS 5	TC2YC2OXP	C3.COOH → C2CyCOC + OH
TS 6	TC2CJ*CXQ	C2C=C + HO_2 → C2C.COOH
TS 7	TC2YCCOXP	C2C.COOH → C2CyCOC + OH
TS 8	TC2YCCQ	C2C.COOH → C2CCOO.
TS 9	TC2YC*CXQ	C2CCOO. → C2C=C + HO_2
TS 10	TCYCCQC	C2CCOO. → C2.CCOOH
TS 11	TC2YCCQO	C2C(OH)COO. → C2C(O.)COOH
TS 12	TICPYCCQC	C2C(OH)COO. → C2.C(OH)COOH
TS 13	TC2CPYCQ	C2C(OH)COO. → C2C(OH)C.OOH
TS 14	TICCQYCPC	C2C(O.)COOH → C2.C(OH)COOH
TS 15	TC2YCPCIQ	C2C(O.)COOH → C2C(OH)C.OOH
TS 16	TICPYC3OXP	C2.C(OH)COOH → CCyC3O(OH) + OH
TS 17	TC2YCQOC	C2C(OO.)COH → C2C(OOH)CO.
TS 18	TICCPYCQC	C2C(OO.)COH → C2.C(OOH)COH
TS 19	TC2YCQCIP	C2C(OO.)COH → C2C(OOH)C.OH
TS 20	TICCQYCQC	C2C(OO.)COOH → C2.C(OOH)COOH
TS 21	TC2YCQOOC	C2C(OO.)COOH → C2C(OOH)COO.
TS 22	TC2YCQCIQ	C2C(OO.)COOH → C2C(OOH)C.OOH
TS 23	TICQYCCQC	C2C(OOH)COO. → C2.C(OOH)COOH
TS 24	TC2*CYCQ	C=C(C)COO. → C=C(C)C.OOH
TS 25	TC*YCCQC	C=C(C)COO. → C=C(C.)COOH
TS 26	TC2*YCOOC	C=C(C)COO. → C2.CyCOOC
TS 27	TCYC*COOC	C=C(C)COO. → CCyC.COOC
TS 28	TC*YC3OXP	C=C(C.)COOH → C=CyCCOC + OH

The first 10 transition states are related to C3C. dissociation, C3C. + O_2, C2C=C + HO_2, the next 9 transition states are for (C2C=C)-OH + O_2 and the following 4 are for (C2C=C)-OOH + O_2 sub system. The last 5 transition states are related to C2.C=C + O_2

sub system. These are important reactions for the further oxidation of C2C=C to secondary products and will be described in the following sections.

Thermodynamic properties of transition states are listed in Appendix IIB. 1. The transition state structures and corresponding internal atom bond lengths are showed in Appendix IIB. 2-4 along with frequencies, moment of inertia for transition states of MTBE and CH_3OH dissociation in IIB. 2, IIB. 4 respectively, and important thermodynamic reaction analysis information for C2C=C related reactions in IIB. 3. The values of A and n from thermodynamic analysis have been used as high pressure limit input parameters for each corresponding reactions above. While the E_a are still estimated using the methods described in chapter 2 with ΔH or ΔU from thermodynamic reaction analysis (performed by using computer program THERMRXN) which be also shown in IIB. 3.

8.4 Quantum RRK Analysis of Important Pathways

QRRK analysis are performed for all chemical activation and unimolecular dissociation pathways in MTBE system. The QRRK input parameters and reference sources are listed in Appendix IID. 1-86 along with potential energy level diagrams. The most important pathways, abstraction and unimolecular dissociation of MTBE, oxidation of iso-butene, and dissociation of methanol, are described below.

8.4.1 Abstraction and Dissociation Reactions of MTBE

8.4.1.1 Abstraction Reaction of MTBE

In the MTBE + O_2 + Ar atmosphere, the initial reactions are H abstraction of MBTE by O_2 as well as O, H, OH, and HO_2 radicals or atoms, or thermal dissociation reactions at

relatively high temperatures (> 900 K) There are two types of hydrogen on MTBE, the methyl-ether group H, C3COC--H, and tert-butyl-ether group H, H--C3COC. The C-H bond (or CH_2 – H bond) strengths of the methyl-ether group on MTBE are approximately 97 5 kcal-mol^{-1}, which is similar to a tertiary C-H bond (96.3 kcal-mol^{-1}), thus it can be easily abstracted by a number of other radicals. The C-H bond strengths of the tert-butyl-ether group on MTBE is about the same as a C-H bond on neo-C5 (101.1 kcal-mol^{-1}). Two types of hydrogen on MTBE can be abstracted by atoms, radicals and molecular O_2:

	Reactions	k (cm^3 mol^{-1} s^{-1})
R 8-1	C3COC + O → C3COC. + OH	$5.351 \times 10^{12}\ T^0 \exp(-3.031$ kcal-mol^{-1} /RT)
R 8-2	C3COC + O → C3.COC + OH	$1.53 \times 10^{9}\ T^{1.5} \exp(-5.305$ kcal-mol^{-1} /RT)
R 8-3	C3COC + H → C3COC. + OH	$7.2 \times 10^{8}\ T^{1.5} \exp(-4.3515$ kcal-mol^{-1} /RT)
R 8-4	C3COC + H → C3.COC + OH	$2.16 \times 10^{9}\ T^{1.5} \exp(-6.997$ kcal-mol^{-1} /RT)
R 8-5	C3COC + OH → C3COC. + H_2O	$6.27 \times 10^{9}\ T^0 \exp(-0.739$ kcal-mol^{-1} /RT)
R 8-6	C3COC + OH → C3.COC + H_2O	$1.08 \times 10^{7}\ T^{2.0} \exp(-0.525$ kcal-mol^{-1} /RT)
R 8-7	C3COC + HO_2 → C3COC. + H_2O_2	$9.64 \times 10^{10}\ T^0 \exp(-14.536$ kcal-mol^{-1} /RT)
R 8-8	C3COC + HO_2 → C3.COC + H_2O_2	$3.01 \times 10^{4}\ T^{2.55} \exp(-15.5$ kcal-mol^{-1} /RT)
R 8-9	C3COC + CH_3 → C3COC.+ CH_4	$1.31 \times 10^{0}\ T^{4.0} \exp(-11.567$ kcal-mol^{-1} /RT)
R 8-10	C3COC + CH_3 → C3.COC + CH_4	$1.36 \times 10^{0}\ T^{3.65} \exp(-7.154$ kcal-mol^{-1} /RT) cm^3 mol^{-1} s^{-1}
R 8-11	C3COC + CH_3O → C3COC.+ CH_3OH	$3.01 \times 10^{11}\ T^0 \exp(-5.266$ kcal-mol^{-1} /RT)
R 8-12	C3COC + CH_3O → C3.COC + CH_3OH	$9.03 \times 10^{11}\ T^0 \exp(-7.866$ kcal-mol^{-1} /RT)
R 8-13	C3COC + O_2 → C3COC. + HO_2	$2.05 \times 10^{13}\ T^0 \exp(-38.392$ kcal-mol^{-1} /RT)
R 8-14	C3COC + O_2 → C3.COC + HO_2	$4.04 \times 10^{13}\ T^0 \exp(-39.432$ kcal-mol^{-1} /RT)

We use Dean and Bozzelli's method described in chapter 2 to calculate a rate of 1.53 × 10^9 $T^{1.5}$ exp(-5.305 kcal-mol^{-1} /RT) cm^3 mol^{-1} s^{-1} for reaction (R 8-2). The NIST fitted value of 5.351 × 10^{12} T^0 exp(-3.031 kcal-mol^{-1} /RT) cm^3 mol^{-1} s^{-1} for reaction COC + O → COC. + OH is used for the rate of reaction (R 8-1).

The rates for reaction (R 8-3,4,6,10) are calculated using Dean and Bozzelli's method described in chapter 2. The rate of reaction (R 8-5) is taken directly to be that of COC + OH → prod (86 ATK). The A factor of reaction (R 8-7) is taken to be that of CH_3OH + HO_2 → CH_2OH + H_2O_2 (87 TSA), and E_a is taken as the average of the E_a of above reaction (E_a = 12.579 kcal mol^{-1}) and the reaction CCC + HO_2 → CCC. + H_2O_2 (E_a = 16.494 kcal mol^{-1}, 88 TSA). The rate constant of reaction (R 8-8) is taken to be that of C3C + HO_2 → C3.C + H_2O_2 (90 TSA).

CH_3 radical plays an important role in the MTBE decay, especially in the pyrolysis case. The fitted value from NIST for COC + CH_3 → COC. + CH_4 and the calculation value from Dean and Bozzelli's method were used for reaction 9 (R 8-9) and 10 (R 8-10) respectively. The current values of rates used for these two reactions are directly taken from 90 ZHA/BAC of NIST (National Institute of Standard Technology Database) for reaction 9 (R 8-9) and 90 TSA for C3C + CH_3 → C3.C + CH_4 respectively. The lower rates of NIST give better modeling results to fit experimental data.

The A factor for reaction 11 (R 8-11) is taken that of CH_3OH + CH_3O → CH_2OH + CH_3OH (87 TSA), and E_a is taken as the average of the E_a of above reaction (E_a = 4.074 kcal mol^{-1}) and the reaction CCC + CH_3O → CCC. + CH_3OH (E_a = 6.458 kcal mol^{-1}, 88 TSA). Taking reaction 11 (R 8-11) as a reference, we use Dean and Bozzelli's method to

calculate the rate constant of reaction 12 (R 8-12) as $k = n_H A^n \exp(-[E_{ref.} - f(\Delta H_{ref.} - \Delta H)] / RT$ cm^3 mol^{-1} s^{-1}. The number of abstractable hydrogen $n_H = 9$, A is from reference reaction ($A/(per\ H) = A_{(R\ 8\text{-}21)} / 3 = 3.01 \times 10^{11} / 3 = 1.003 \times 10^{11}$), and $E_a = 5.266 - 0.65$ [-7.56 - (-3.5)] = 7.866 kcal mol^{-1}. The f is taken as that of CH_3 radical.

The abstraction reactions between MTBE and O_2 are initial reaction and very important in the oxidation of MTBE system. Two sets of rate values for reaction 13 (R 8-13) and reaction 14 (R 8-14) are tested in this study. A literature data of 4.04×10^{13} T^0 exp(-50.932 kcal-mol^{-1} /RT) cm^3 mol^{-1} s^{-1} (90 TSA for C3C + O_2 → C3.C + HO_2) for reaction 13 (R 8-13), and an evaluated rate constant of 2.05×10^{13} T^0 exp(-47.892 kcal-mol^{-1} /RT) cm^3 mol^{-1} s^{-1} for reaction 14 (R 8-14), (based on two reference reaction: CCC + O_2 → CCC. + HO_2, 3.97×10^{13} T^0 exp(-50.872 kcal-mol^{-1} /RT) cm^3 mol^{-1} s^{-1}, 88 TSA. CH_3OH + O_2 → CH_2OH + HO_2, 2.05×10^{13} T^0 exp(-44.911 kcal-mol^{-1} /RT) cm^3 mol^{-1} s^{-1}, 87 TSA), are tested and modeling results suggest the higher values should be used for these two reactions. The alternative E_a's, 38.392 kcal-mol^{-1} for reaction 13 (R 8-13) and 39.432 kcal-mol^{-1} for reaction 14 (R 8-14), are estimated based on the recent evaluated activation energies: 38.56 kcal-mol^{-1} for reaction C2C=C + O_2 → C2.C=C + HO_2, and 39.11 kcal-mol^{-1} for reaction CC=C + O_2 → C.C=C + HO_2, by Walker research group, which lead to faster reaction than corresponding NIST evaluation. This set of rate constant gives reasonable modeling results.

8.4.1.2 Unimolecular Dissociation of MTBE

The Unimolecular decomposition reactions of MTBE are initial reactions in MTBE pyrolysis and become possible and more important initial reactions in MTBE oxidation at

higher temperatures. The energy diagram and input parameters with reference sources for unimolecular dissociation calculations on the decomposition reactions of MTBE are detailed in Appendix IID 1. There are six possible product channels as following:

R 8-15	C3COC → C2C=C + CH_3OH	ΔH_{rxn} = 15.19 kcal mol^{-1}
R 8-16	C3COC → C3CO. + CH_3	ΔH_{rxn} = 80.08 kcal mol^{-1}
R 8-17	C3COC → C2C.OC + CH_3	ΔH_{rxn} = 82.45 kcal mol^{-1}
R 8-18	C3COC → C3C. + CH_3O	ΔH_{rxn} = 82.55 kcal mol^{-1}
R 8-19	C3COC → C3COC. + H	ΔH_{rxn} = 97.90 kcal mol^{-1}
R 8-20	C3COC → C3.COC + H	ΔH_{rxn} = 100.96 kcal mol^{-1}

ΔH_{rxn} values are at average temperature from 300 K to 1500 K. The rates of these channels at 873 K and 1123 K are:

		$k_{873\,K}$ (s^{-1})	$k_{1123\,K}$ (s^{-1})
R 8-15	C3COC → C2C=C + CH_3OH	1.056×10^{-1}	8.158×10^{1}
R 8-16	C3COC → C3CO. + CH_3	1.769×10^{-4}	7.967×10^{-1}
R 8-17	C3COC → C2C.OC + CH_3	3.206×10^{-5}	9.641×10^{-2}
R 8-18	C3COC → C3C. + CH_3O	3.614×10^{-4}	2.122×10^{0}
R 8-19	C3COC → C3COC. + H	1.000×10^{-9}	3.187×10^{-5}
R 8-20	C3COC → C3.COC + H	1.000×10^{-9}	6.119×10^{-5}

The rate constants and the sources for these reactions are listed in Appendix IID. 1.

The most important product channel is iso-butene and methanol formation pathway. The four-center transition state for this reaction had been proposed from several literature references (see chapter 6). We use semi-empirical MOPAC PM3 to define the transition state for this elimination reaction and confirm the four center elimination mechanism. The important information about this transition state is listed in Appendix IIB. 2. One of three methyl carbons on MTBE (C3COC) is ready to lose one of three H attached on it, this methyl H attach to oxygen to get ready to be hydroxyl H for methanol and compose two of four bonds for transition ring C---H---O. The tetra C on MTBE (C3COC) collect one electron from methyl C (lose H) and the other one from oxygen by break C-O bond to

form a π bond, thus double bond for forming iso-butene, this compose the other two bonds of transition ring O---C==C. In this four member transition ring (tC)==pC---H---O---tC (tC means tetra C, pC means primary C), the forming carbon double bond has a 1.440 Å of bond length, longer than regular carbon double bond length, 1.334 Å, in iso-butene, and shorter than regular single carbon bond, 1.539 Å, in MTBE. The other forming O-H bond has a 1.143 Å of bond length while a regular O-H bond in methanol has a 0.949 Å of bond length. The breaking C-O bond, making it possible to form methanol directly from MTBE, has a 1.657 Å of bond length, much longer than normal C-O bond, 1.442 Å, in MTBE. The last bond in the four member transition ring is C-H bond, breaking to take methyl-H away from forming iso-butene and give it to forming methanol as a hydroxy-H to close the formation of two separated species from MTBE. This breaking C-H bond length is found, 1.529 Å, much much longer than methyl-H bond length, 1.098 Å, in MTBE. The bond lengths in four member transition ring shows a loose transition structure which gives a relative high A factor and low E_a for this reaction. All other bonds besides transition ring are only having little change, 0.01-0.02 Å.

Other reaction paths of MTBE dissociation give intermediate radical, C3COC., C3.COC, C2C.OC, C3CO., which all rapidly undergo further dissociation to give C2C=C, C2C=O, CC=C, CH_2O; radicals C3C., CH_3, CH_3O and other species (see detailed pathways in Appendix IID. 2-3 and 11).

8.4.1.3 C3C. + O_2 → Products

There are several important radical products from high temperature, unimolecular dissociation of MTBE, tertiary butyl and methoxy radicals from dissociation of MTBE

(C3COC) to C3C. + CH_3O (ΔH_{rxn} = 82.55 kcal mol^{-1}), and tert-butoxy plus methyl radicals from C3COC → C3CO. + CH_3 (ΔH_{rxn} = 80.08 kcal mol^{-1}).

T-butyl radical C3C. is an important intermediate radical from MTBE dissociation, it can also form from dissociation of C3COC. radical and H atom addition to C2C=C. The C3C. radical is relatively more stable than other intermediate radicals because of its tertiary structure and because its beta scission reaction all require scission of primary C---H bond rather than a weaker C---C bond or C---O bond, it can accumulate up to a relative high concentration level in the intermediate temperatures. The C3C. radical can lose a H to form iso-butene (Appendix IID. 4) via beta scission reaction. The C3C. can also react with O_2 to form chemically activated energized adduct $[C3COO.]^*$, which can be stabilized or undergo isomerization reaction via a intramolecular H transfer and this alkyl hydroperoxide radical (C3.COOH) can further react by addition to an oxygen or by β-scission reaction to C2CyCOC + OH, C2C=C + HO_2 and C=C(C)OOH + CH_3 (see Appendix IID. 5), C=C(C)OOH will rapidly dissociate to C2.C=O radical (Appendix IID. 6). The chemically activated adduct $[C3COO.]^*$ can also eliminate one HO_2 radical directly to form iso-butene. Transition states are found for the isomerization and elimination reactions separately (see Appendix IIB. 3, TS2 and TS3).

Bond lengths in transition states for four related reactions (C3COO. → C2C=C + HO_2; C3COO. → C3.CCOOH, C3.CCOOH → C2C=C + HO_2, C3.CCOOH → C2CyCOC + OH) are listed in Appendix IIB. 2 - 5). Transition states show that C3COO. radical can undergo isomerization to alkyl hydroperoxide radical C3.CCOOH, or eliminate one HO_2 directly from C3COO. radical via two different transition states [95], and hydroperoxide

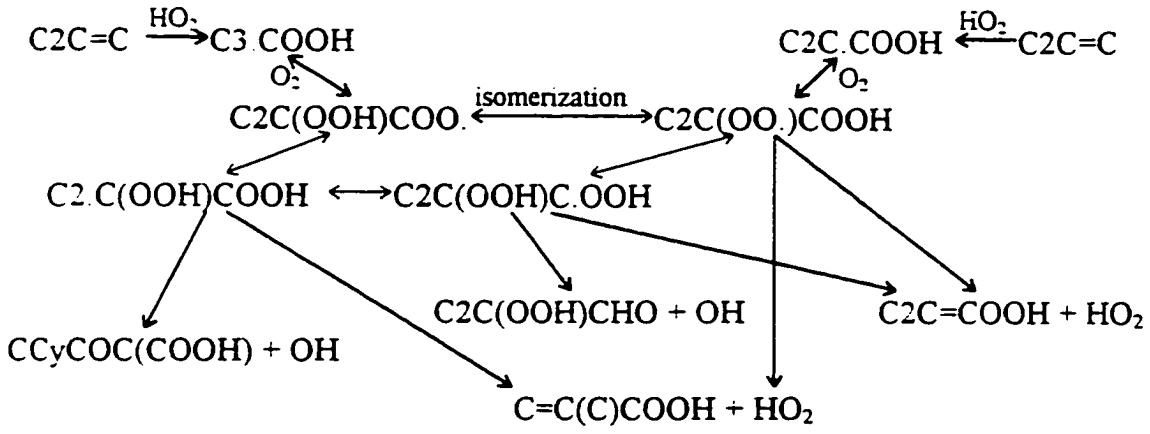
isomer C3 COOH then undergoes β-scission to C2C=C + HO_2, or to epoxide C2CyCOC + OH via different transition states. In the transition state for isomerization reaction (IIB. 3, TS 2), two "unusual" bonds are involved, one is breaking bond C-H which has a 1.266 Å bond length instead of normal bond length 1.098 Å, the other is forming bond O-H which has a 1.321 Å bond length instead of normal bond length 0.943Å. In the transition ring for HO_2 direct elimination (IIB. 3 - TS 3), four bonds are involved. The breaking C-H bond and forming O-H bond similar to isomerization transition ring, that the C-O bond length is extended to 2.030 Å from 1.497Å indicates a breaking; the C-C bond reduces to a 1.404 Å from 1.527 Å, which indicates two electrons from C-H breaking bond and C-O breaking bond is forming a π double bond for C=C. In the transition state for reaction C3.COOH → C2C=C + HO_2 (Appendix IIB. 4), C3.C---OOH bond is extended to 1.923 Å from 1.431 Å, C3CO---OH bond here is 1.351 Å, while in the transition state for reaction C3.COOH → C2CyCOC + OH (Appendix IIB. 5), C3.C---OOH bond is 1.477 Å and C3CO---OH is extended to 1.679 Å from 1.514 Å. In addition to these two bonds involved in the transition state for reaction C3.COOH → C2CyCOC + OH (Appendix IIB. 5), a new C---O bond in the length of 1.779 Å is being formed to close the three member ring for C2CyCOC.

The reaction of O_2 addition to C3C. and further dissociation of peroxy and/or hydroperoxide radicals is an important reaction system in the oxidation of the MTBE intermediate C3C. at low to mid range temperatures up to 1300 K since both O_2 and C3C. are present at relative high levels. The products from C3C. + O_2 are C2C=C, C2CyCOC and C2.C=O radical, along with HO_2, CH_3 and OH radicals.

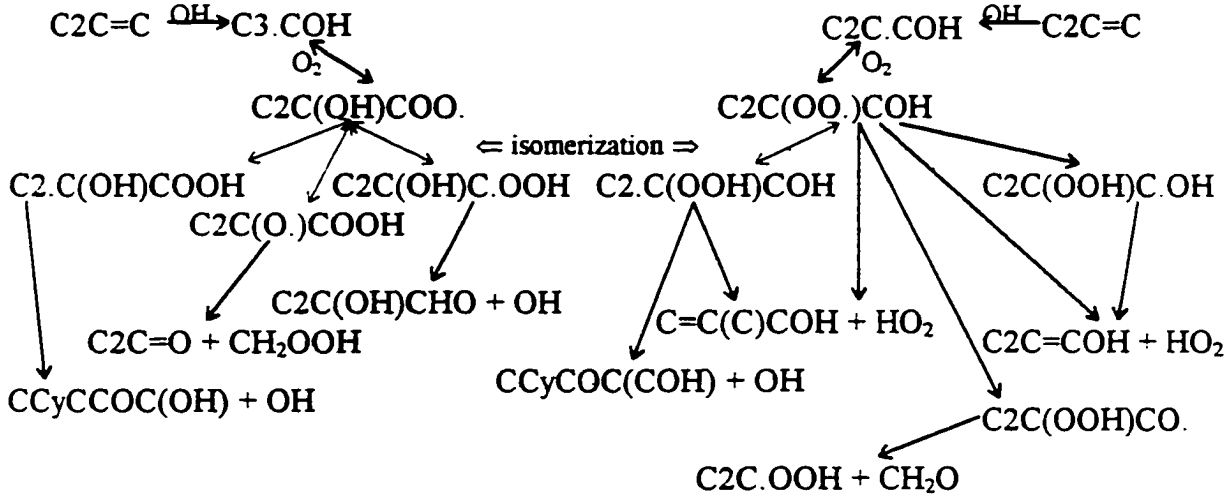
8.4.2 Oxidation of Iso-Butene

Iso-butene is a noted major product from MTBE oxidation and pyrolysis as demonstrated from all reported experiments done by several groups [84 93]. As discussed above, iso-butene can be formed from directly dissociation of MTBE (C3COC → C2C=C + CH_3OH), dissociation of intermediate radicals C3.COC (C3.COC → C2C=C + CH_3O), C3C. (C3C. → C2C=C + H) and also from O_2 addition to C3C. radical. Further oxidation of iso-butene is important on the explanation of important, secondary product formation.

One of the 6 allylic H can be abstracted from iso-butene by OH, O, H, CH_3 and other radicals to form allylic iso-butenyl radical, which can react with O_2, see section 8.4.2.4. Direct dissociation reaction of iso-butene can occur at high temperatures. (Appendix IID. 7) to form CC.=C + CH_3 (ΔH_{rxn} = 97.46 kcal-mol^{-1}), the CC.=C then (Appendix IID. 8) either dissociate to C=C=C + H, or isomerize to allyl radical (C=CC.), which can react with O_2 (Appendix IID. 68), like C2.C=C does (see section "8.4.2.4"). The most important reaction pathways for iso-butene oxidation are additions of OH and HO_2 radicals to form hydroxyl and peroxy radicals, these intermediate radicals can further react with O_2 as follows:



And



We discuss abstraction reactions of iso-butene first, then OH, HO_2 and O_2 addition reactions (C2C=C + OH/HO_2, + O_2) and the further reactions of secondary important products from those addition reactions, and complete the iso-butene oxidation with the reaction of allylic iso-butenyl radical with O_2.

8.4.2.1 Reactions between C2C=C and OH, O, H, CH_3, CH_3O, HO_2, O_2

The abstraction reaction of iso-butene is important not only because of C2C=C's relatively high concentration levels but also the resonance stabilized structure of allylic iso-butenyl radical. The dissociation energy of weakly allylic C-H bond on C2C=C is only 88.2 kcal-mol^{-1}, which is ca 12.9 kcal-mol^{-1} less than normal C-H bond on alkane. The 6 allylic H can be abstracted by OH, H, O, etc. reactive radicals, also by intermediate reactive radical or molecule such as HO_2 and O_2. We consider the following abstraction reactions of C2C=C in this system.

	Reactions	k (cm^3-mol^{-1}-s^{-1})
R 8-21	C2C=C + O → C2.C=C + OH	$1.21 \times 10^{11}\ T^{0.7}$ exp(-7.633 kcal-mol^{-1} /RT)
R 8-22*	C2C=C + O → C2CyCOC	$4.20 \times 10^{12}\ T^{0}$ exp(-0.503 kcal-mol^{-1} /RT)
R 8-23	C2C=C + H → C2.C=C + H_2	$3.50 \times 10^{5}\ T^{2.5}$ exp(-2.492 kcal-mol^{-1} /RT)
R 8-24	C2C=C + H → CC=C + CH_3	$1.45 \times 10^{13}\ T^{0}$ exp(-1.302 kcal-mol^{-1} /RT)
R 8-25	C2C=C + OH → C2.C=C + H_2O	$6.24 \times 10^{6}\ T^{2.0}$ exp(-(-0.298)) kcal-mol^{-1} /RT)
R 8-26	C2C=C + CH_3 → C2.C=C + CH_4	$4.42 \times 10^{0}\ T^{3.5}$ exp(-5.675 kcal-mol^{-1} /RT)
R 8-27	C2C=C + CH_3O → C2.C=C + CH_3OH	$4.42 \times 10^{0}\ T^{3.5}$ exp(-5.675 kcal-mol^{-1} /RT)
R 8-28	C2C=C + HO_2 → C2.C=C + H_2O_2	$1.93 \times 10^{4}\ T^{2.6}$ exp(-13.91 kcal-mol^{-1} /RT)
R 8-29*	C2C=C + HO_2 → C2CyCOC + OH	$1.05 \times 10^{12}\ T^{0}$ exp(-14.206 kcal-mol^{-1} /RT)
R 8-30	C2C=C + O_2 → C2.C=C + HO_2	$4.79 \times 10^{12}\ T^{0}$ exp(-38.56 kcal-mol^{-1} /RT)

* reaction (R 8-22) is a n addition reaction and reaction (R 8-29) is an addition and then epoxide formation reaction.

There are no available data for reaction (R 8-21) C2C=C + O → C2.C=C + OH. The rate constant of $6.03 \times 10^{10}\ T^{0.7}$ exp (7.633 kcal-mol^{-1} / RT) cm^3-mol^{-1}-s^{-1} for reaction CC=C +

O → C.C=C + OH (91 TSA) had been taken as reference and multiplied by a factor of 2 is considering 6 allylic H on C2C=C while 3 allylic H on CC=C. A triplet O atom can also add to carbon double, via "triplet → singlet" conversion by collision, to form 2,2-dimethyloxerine which is a important product from oxidation of C2C=C. The rate constant is also referenced from reaction O + CC=C → CCyCOC (73 HER).

The H atom can abstract one allylic H from C2C=C to form C2.C=C radical similar to reaction CC=C + H → H_2 + C.C=C, which has a rate constant of 1.73×10^5 $T^{2.5}$ exp (2.492 kcal-mol^{-1} / RT) cm^3-mol^{-1}-s^{-1} (91 TSA). We use this rate constant by timing a factor of 2. The H can also replace a methyl radical from C2C=C to form CC=C + CH_3, a rate constant of reaction CC=C + H → CH_3 + C=C is used by multiplying by a factor of 2.

The OH radical is other most important one in the oxidation reaction systems. One report in literature data is from Walker's group [96]. A rate constant of 7.80×10^{12} T^0 exp (0.0 kcal-mol^{-1} / RT) cm^3-mol^{-1}-s^{-1} (78 BAK/BAL) was obtained using relative rate technique at 0.658 atm and one temperature, 753 K in N_2 bath. Considering wide range of temperature, we choose data for propene and multiplied by a factor of 2 for the increased number of H's.

The CH_3 as well as CH_3O radical can accumulate to relatively high concentration level. The abstraction of allylic H on C2C=C by CH_3 or CH_3O is considered to be analogous to abstraction reaction by CH_3 or CH_3O from CC=C. A factor of 2 is multiplied to account for 6 allylic H on C2C=C.

The HO_2 radical is not as an strong abstracting agent as O, OH or H because the HOO --- H bond is only 88 kcal-mol^{-1}. HO_2 exists in relative high concentrations at moderate

temperature, up to 1200 K in oxidation environments especially in intermediate temperature range 600 K to 1000K. The abstraction of allylic H from C2C=C is compete with the reaction of addition of peroxy radical to carbon double bond, epoxide formation and the releasing of OH radical. The propene's data are taken as reference data for both reactions of iso-butene.

The abstraction reaction between C2C=C and O_2 is considered in this system because both species are present at high concentrations. Walker's group conducted a series of O_2 abstraction reaction studies and found a rate constant of 4.79×10^{12} T^0 exp (38.56 kcal-mol^{-1} / RT) cm^3-mol^{-1}-s^{-1} for C2C=C and of 1.95×10^{12} T^0 exp (39.11 kcal-mol^{-1} / RT) cm^3-mol^{-1}-s^{-1} for CC=C, which is much faster than NIST data of 6.03×10^{13} T^0 exp (47.59 kcal-mol^{-1} / RT) cm^3-mol^{-1}-s^{-1} for CC=C at intermediate temperature. We chose Walker's data.

8.4.2.2 C2C=C + HO_2 → C3.COOH/C2C.COOH, + O_2 → Products

The C2C=C + HO_2 reaction system becomes more important in the intermediate temperature because of high concentration of C2C=C and HO_2 produced from MTBE dissociation and further reactions of resulted intermediate radicals. The HO_2 radical can attach to either side of carbon double bond on C2C=C and results in two peroxy radicals C3.COOH and C2C.COOH. Both of these two radicals can form 2,2-dimethyloxirane by releasing one OH radical, or undergo isomerization reaction via intramolecular H transfer and further β-scission or HO_2 elimination reactions. C3.COOH radical is also formed from C3COO. isomer via C3C. + O_2 (we discussed above), which shows a reverse reaction chain: C2C=C + HO_2 ⇔ C3.COOH ⇔ C3COO. ⇔ C3C. + O_2. An equilibrium

exists between both molecules (C2C=C, O_2) and radicals. The potential energy level diagrams of C2C=C + HO_2 → C3.COOH → products (Appendix IID. 9) show the chemical activation reaction system for C2C=C + HO_2, and the C3.COOH radical can be formed from both C2C=C + HO_2 and C3C. + O_2.

The potential energy level diagram in Appendix IID. 10 shows the addition of HO_2 to the terminal carbon (CD/H_2 carbon) of double bond in C2C=C. Several product channels exist for further reactions of C2C.COOH since there are 4 types of H on C2C.COOH. These hydrogens can be transferred to form different isomers, one of the isomers being C2CCOO. radical, which can eliminate directly H-O-O group (as HO_2) just like C3COO. radical we discussed in section 8.4.1.3. An equilibrium, C2C=C + HO_2 ⇔ C2C.COOH ⇔ C2CCOO. ⇔ C3.C + O_2, may not exist for C2C.COOH because of low concentration level of C3.C radical. The potential energy level diagrams of C2C.COOH (Appendix IID. 10) shows that: 2,2-dimethyloxirane (C2CyCOC) formation from C2C.COOH, C2C=C formation with HO_2 elimination directly from C2CCOO. isomer, and methyloxetane (CCyCCOC) formation are important product channels.

The reactions of O_2 addition to both C3.COOH and C2C.COOH radicals (Appendix IID. 11-12) are important in the high O_2 environment. The resulting intermediate radicals C2C(OOH)COO., C2C(OO.)COOH, C2.C(OOH)COOH and C2C(OOH)C.OOH undergo HO_2 direct elimination reaction, isomerization and epoxide formation, HO_2 β-scission and CH_3 elimination reactions, to form products CCyCOC(COOH), C2C=COOH, C=C(C)COOH and C2C(OOH)CHO, which further reactions will be discussed in section

8.4.2.4. An equilibrium exist in C3.COOH + O_2 ⇔ C2C(OOH)COO. ⇔ C2C(OO.)COOH ⇔ C2C.COOH + O_2 system.

8.4.2.3 C2C=C + OH → C3.COH/C2C.COH, + O_2 → Products

The addition of OH to C2C=C produces important stabilized intermediates C3.COH and C2C.COH. The potential energy level diagram (Appendix IID. 13) shows that chemically activated adduct $[C3.COH]^*$ has enough energy to go directly to C=C(OH)C, which is the end isomer of C2C=O. The acetone product C2C=O + CH_3, via C3CO. isomer becomes more important at higher temperatures since adduct $[C3.COH]^*$ is more exothermic and this channel needs ca 10 kcal-mol^{-1} more energy. The direct dissociation to products from energized $[C2C.COH]^*$ adduct are less important (see Appendix IID. 14).

The stabilized or energized C3.COH radical can both react with O_2 to form $[C2C(OH)COO.]^*$ adduct, which can directly go to products: C2C=O + CH_2OOH via C2C(O.)COOH isomer; CCyCCOC(OH) + OH via C2.C(OH)COOH isomer; C2C(OH)CHO + OH via C2C(OH)C.OOH isomer (see Appendix IID. 15), in addition to stabilized to C2C(OH)COO. radical. The further reactions of CCyCCOC(OH) and C2C(OH)CHO will discussed in section 8.4.2.4.

The chemically activated adduct $[C2C(OO.)COH]^*$ from reaction of C2C.COH with O_2 can be stabilized to C2C(OO.)COH radical, or dissociate to products C2C=COH + HO_2 via the C2C(OOH)C.OH isomer, to products CCyCOC(COH) + HO_2 and C=C(C)COH + HO_2 via C2.C(OOH)COH isomer, to products C2C.OOH + CH_2O via C2C(OOH)CO. isomer, or undergo direct HO_2 elimination to C=C(C)COH / C2C=COH. The C2C.OOH will rapidly dissociate to C2C=O + OH (see Appendix IID. 26). The potential energy

level diagram (Appendix IID. 16) shows all the above product channels are important since the dissociation back to reactants had the highest activation energy, that is, the adduct has enough energy to go directly to products.

8.4.2.4 Further Reactions of Intermediates from Iso-Butene Oxidation

The important intermediates from the very exothermic product channels of the iso-butene oxidation reaction system (C2C=C + OH/HO_2, + O_2) are C2C=COOH, C=C(C)COOH, C2C(OOH)CHO, C2C(OH)CHO, CCyCOC(COH) and CCyCOC(COOH). The potential energy level diagrams are shown in Appendix IID. 17-25. All these species can undergo β-scission reactions as discussed below.

C2C=COOH produces, (see Appendix IID. 17), an OH + C2C=CO., the C2C=CO. radical instantly rearranges to C2C.CHO radical. The reactions of C2C.CHO is discussed later in this section. C=C(C)COOH, see Appendix IID. 18, produces an OH + C=C(C)CO., the C=C(C)CO. radical can further undergoes dissociation to C=C(C)CHO (Appendix IID. 19), an important minor product found from experiments, by losing a H, or undergoes beta scission to CC.=C + CH_2O, which is higher in E_a than H atom elimination.

Decomposition of both C2C(OOH)CHO and C2C(OH)CHO (Appendix IID. 20-21) produce C2C.CHO radicals by elimination of OH or HO_2 radical. The C2C(OOH)CHO have the other product channel C2C.OOH + CHO, C2C(O.)CHO + OH, the C2C.OOH quickly dissociate to C2C=O + OH (Appendix IID. 26) and the C2C(O.)CHO dissociate to C2C=O + CHO. The alternative product channel from C2C(OH)CHO is C2C.OH + CHO. The C2C.CHO radical can either dissociate to CC.C + CO via isomerization to

C2CC.=O, or react with O_2 to give product C=C(C)CHO, C2C=C=O, C2C=O and CO, the reactions related to the C2C.CHO radical will discuss later in section 8.4.2.6.

Both CCyCOC(COOH) and CCyCOC(COH) will decompose to CCyC.OC (Appendix IID. 24-25), and then to C2.C=O (Appendix IID. 27). Two steps are needed for CCyC.OC radical formation from CCyCOC(COOH) by first releasing OH to form CCyCOC(CO.) radical, then eliminating CH_2O (beta scission) from CCyCOC(CO.) radical (Appendix IID. 24).

8.4.2.5 Stable Molecules C2CyCOC, C2C=O and C=C(C)CHO

The most stable secondary products are C2CyCOC, C2C=O and C=C(C)CHO from oxidation of C2C=C. At high temperature, these species can thermally decompose to CCyC.OC + CH_3 from C2CyCOC (Appendix IID. 28); to $CH_3C.=O$ + CH_3 from C2C=O (Appendix IID. 29); to C=C(C)C.=O + H and CC.=C + CHO from C=C(C)CHO (Appendix IID. 30). At low and intermediate temperatures, these species can undergo abstraction reactions to form C2CyCOC., C2.C=O and C=C(C)C.=O. The C2CyCOC. then undergoes isomerization reaction to C2C.CHO radical (see Appendix IID. 33), C2.C=O can further dissociate to C=C=O + CH_3 (see Appendix IID. 32), and C=C(C)C.=O can eliminate CO molecule with CC.=C radical (see Appendix IID. 31). The CCyC.OC radical from thermal decomposition of C2CyCOC will rapidly isomerize to C2.C=O radical (see Appendix IID. 27). The $CH_3C.=O$ radical from C2C=O will rapidly decompose to CH_3 + CO. The C=C(C)C.=O radical from C=C(C)CHO via abstraction reactions with radical pool or decomposition reaction at high temperatures will further dissociate to CO + CC.=C. The CC.=C from both C=C(C)CHO molecule and

C=C(C)C.=O radical have relative more reaction pathways, one of the most important is CC.=C radical reacts with O_2 (see section 8.4.4)

In summary, these stable species can convert to CH_3, CO, H, CC.=C, C2C.CHO radical and C=C=O.

8.4.2.6 C2C.CHO and C2C.CHO + O_2

The radical C2C.CHO can be formed in several ways. The ring opening (β-scission) reaction of C2CyCOC. radial is the major source for C2C.CHO formation here. It can also be formed from unimolecular decomposition of C2C=COOH, C2C(OOH)CHO, C2C(OH)CHO, and by abstraction reactions. The potential energy level diagram (Appendix IID. 33) shows that the C2C.CHO radial can undergoes unimolecular dissociation reaction or isomerization reaction followed by further β-scission reaction to CC.C + CO at high temperatures. C2C.CHO radical will also react with O_2. This O_2 addition reaction is much more important at low and intermediate temperatures and fuel lean conditions (see Appendix IID. 34). The favored low energy products from C2C.CHO + O_2 are C=C(C)CHO, C2C=C=O, C2C.OOH (→ C2C=O + OH), HO_2 and CO.

8.4.2.7 Reaction of Allylic Iso-Butenyl Radical with O_2

As noted in the previous discussion, an important secondary product from reactions of iso-butene is allylic iso-butenyl radical C2.C=C, formed from abstraction reactions of iso-butene due to the weakly bonded hydrogen atom (the allylic C-H bond is only 88.3 kcal mol^{-1}). The allylic iso-butene radical C2.C=C could accumulate to higher levels because of its low reactivity which is due to its high resonance stabilization energy. It can

dissociate to C=C=C + CH_3 (Appendix IID. 35), abstract H from other species to form C2C=C, or react with molecule oxygen.

The C2.C=C radical can also recombine HO_2 to form C=C(C)COOH. This reaction becomes more important at the intermediate temperatures, because that the HO_2 concentration becomes sufficiently large. The allylic iso-butenyl radical is resonantly stabilized, and its thermal decomposition and reaction with O_2 are slow (see below). The energy level diagram and input parameters for the chemical activation calculations on allylic iso-butenyl radical + HO_2 are shown in Appendix IID 18-19. The combination of C2.C=C and HO_2 produce a chemically activated adduct $[C=C(C)COOH]^*$, which has sufficient energy (ca 12 kcal more) to decompose to radical C=C(C)CO. + OH radicals. The C=C(C)CO. radical can then loss one H to form methacrolein C=C(C)CHO with 13.54 kcal mol^{-1} activation energy and formaldehyde CH_2O + CC.=C with 23.5 kcal mol^{-1} activation energy.

The addition of O_2 to the allylic iso-butene radical is analyzed in this study by using semi-empirical calculations for transition states of the isomerization reactions. The potential energy level diagram is shown in Appendix IID. 36. The chemically activated energized adduct $[C=C(C)COO.]^*$ can most easily dissociate back to C2.C=C + O_2 but a number of channels with activation energies above that of initial reactant energy are of importance. The important pathways considered in this work are (1) C=C(C)COO. ⇔ C=C(C.)COOH ⇒ C=CyCCOC + OH; (2) C=C(C)COO. ⇔ C=C(C)C.OOH ⇒ C=C(C)CHO + OH; (3) C=C(C)COO. ⇔ CCyC.COOC ⇔ CCyCC.OOC ⇔ CC(CO.)CHO ⇒ CC.CHO + CH_2O; (4) C=C(C)COO. ⇔ CCyC.COOC ⇔ CCyCOC(CO.) ⇒ CCyC.OC + CH_2O; (5)

C=C(C)COO. ⇔ C2.CyCOOC ⇔ C2CyCOOC. ⇔ C2C(O.)CHO ⇒ C2C=O + CHO; (6)

C=C(C)COO. ⇔ C2.CyCOOC ⇔ CCyCOC(CO.) ⇒ CCyC.OC + CH_2O. Almost all product channels are very exothermic and have relatively much higher barriers for isomerization processes. Several of the isomerization channels have similar energies for isomerization reactions and are in competition. The reactivity towards O_2 of C2.C=C will increase with temperature, due to exothermic nature of these channels.

8.4.3 Oxidation and Unimolecular Dissociation Reactions of Methanol

Methanol, as a major product from MTBE oxidation, is mainly formed from MTBE dissociation. Some abstraction reactions also result in methanol production. Compared to iso-butene, methanol has relatively simple reaction pathways to go to the final products CH_4 or CH_2O or CO / CO_2. At the intermediate temperature or low temperature, methanol decays mainly by abstraction reactions while its thermal decomposition also plays important role at the high temperature. The important pathways for methanol decay are discussed below.

8.4.3.1 Abstractions Reactions Involving Methanol

There are two types of hydrogen on methanol, methyl H (H---CH2OH bond energy = 97.5 kcal mol^{-1}) and hydroxy H (CH_3O---H bond energy = 104.0 kcal mol^{-1}). At low temperatures, more CH_2OH than CH_3O can be produced from methanol abstraction reactions by other radicals in the system because of relatively weak C-H bond compared to O-H bond.

	Reactions	k (cm^3-mol^{-1}-s^{-1})
R 8-31	$CH_3OH + O \rightarrow CH_2OH + OH$	$1.72 \times 10^{13}\ T^0\ \exp(-4.914$ kcal-mol^{-1}

R 8-32	$CH_3OH + O \rightarrow CH_3O + OH$	$1.00 \times 10^{13}\ T^0 \exp(-5.129\ \text{kcal-mol}^{-1}/RT)$
R 8-33	$CH_3OH + H \rightarrow CH_2OH + OH$	$3.40 \times 10^{13}\ T^0 \exp(-5.497\ \text{kcal-mol}^{-1}/RT)$
R 8-34	$CH_3OH + H \rightarrow CH_3O + OH$	$4.00 \times 10^{13}\ T^0 \exp(-6.095\ \text{kcal-mol}^{-1}/RT)$
R 8-35	$CH_3OH + OH \rightarrow CH_2OH + H_2O$	$1.35 \times 10^{13}\ T^0 \exp(-1.881\ \text{kcal-mol}^{-1}/RT)$
R 8-36	$CH_3OH + OH \rightarrow CH_3O + H_2O$	$1.00 \times 10^{13}\ T^0 \exp(-1.953\ \text{kcal-mol}^{-1}/RT)$
R 8-37	$CH_3OH + CH_3 \rightarrow CH_2OH + CH_4$	$3.19 \times 10^{1}\ T^{3.2} \exp(-7.172\ \text{kcal-mol}^{-1}/RT)$
R 8-38	$CH_3OH + CH_3 \rightarrow CH_3O + CH_4$	$1.44 \times 10^{1}\ T^{3.1} \exp(-6.935\ \text{kcal-mol}^{-1}/RT)$
R 8-39	$CH_3OH + CH_3O \rightarrow CH_2OH + CH_3OH$	$3.01 \times 10^{11}\ T^0 \exp(-4.074\ \text{kcal-mol}^{-1}/RT)$
R 8-40	$CH_3OH + HO_2 \rightarrow CH_2OH + H_2O_2$	$9.64 \times 10^{10}\ T^0 \exp(-12.579\ \text{kcal-mol}^{-1}/RT)$
R 8-41	$CH_3OH + O_2 \rightarrow CH_2OH + HO_2$	$2.05 \times 10^{13}\ T^0 \exp(-44.911\ \text{kcal-mol}^{-1}/RT)$

The OH, O and H radical or atoms can abstract the two types of H from CH_3OH (R 8-31 to R 8-36). The NIST fit values are used for reaction (R 8-31) and reaction (R 8-35), both of which form CH_2OH radical. The A factors of reaction (R 8-32) and reaction (R 8-36) (form CH_3O radical) are both taken from literature (84 WAR, NIST) while their E_a are calculated based on Bozzelli and Dean's equation using corresponding CH_2OH radical formation reaction (R 8-31, R 8-35) as reference separately. The difference of ΔH_{rxn} between CH_2OH and CH_3O formation reaction are the same as 7.16 kcal-mol^{-1}. The f is estimated as 0.03 and 0.01 for O abstraction and OH abstraction separately. Rate constants of abstractions by H are taken from the NIST database, 81 VAN/VAN and 81 HOY/SIE for reaction (R 8-33), 84 WAR for reaction (R 8-34). The rate constants of other abstraction reaction (R 8-37 to R 8-41) are from the NIST recommended data (87 TSA).

8.4.3.2 Unimolecular Dissociation Reactions of Methanol

The decomposition steps of methanol are estimated by QRRK / beta collision analysis as previous described. The potential energy diagram and high pressure limit rate constants for QRRK analysis are illustrated in Appendix IID. 38.

	Reactions	$\Delta H_{rxn,298\,K}$	E_a (kcal-mol^{-1})
R 8-42	$CH_3OH \rightarrow CH_2O + H_2$	22.00 kcal mol^{-1}	90.11
R 8-43	$CH_3OH \rightarrow HCOH + H_2$	70.56 kcal mol^{-1}	86.97
R 8-44	$CH_3OH \rightarrow {}^1CH_2 + H_2O$	91.65 kcal mol^{-1}	90.33
R 8-45	$CH_3OH \rightarrow CH_3 + OH$	92.30 kcal mol^{-1}	91.03
R 8-46	$CH_3OH \rightarrow CH_2OH + H$	96.50 kcal mol^{-1}	96.52
R 8-47	$CH_3OH \rightarrow CH_3O + H$	104.60 kcal mol^{-1}	103.76

The barriers of reaction (R 8-42 to R 8-44) are taken from the study of Walch [96] using complete-active-space self-consistent-field (CASSCF) / internally contracted configuration-interaction (CCI), Ab Initio calculations. The reverse channel of reaction (R 8-44) is found to have no barrier. The barriers of the reverse of reaction (R 8-42, R 8-43) are calculated as 1.7 and -5.2 kcal-mol^{-1} with respect to the energy level of CH_3 + OH channel (44.3 kcal-mol^{-1}). The barriers of these three reactions are then derived as 93.11, 86.97 and 90.33 kcal-mol^{-1} for reaction R 8-42, R 8-43 and R 8-44 respectively. The A factors are taken from Dean [21, 82]. The rate constants of three simple dissociation reactions are calculated from reverse reactions by MR.

8.4.3.3 Reactions of CH_2OH / CH_3O and CH_2O / CHO

More CH_2OH radical is formed from methanol dissociation because of relatively weak bond H---CH_2OH and three methyl H's compared to the one hydroxyl H. Both radicals can undergo β-scission to form formaldehyde with a barrier of 22.83 kcal-mol^{-1} from CH_3O and 30.99 kcal-mol^{-1} from CH_2OH (Appendix IID. 39).

Because of high concentration level of CH_2OH radical, the reaction system of CH_2OH + O_2 plays an important role in the methanol decay to formaldehyde. The potential energy level diagram with QRRK input parameters are listed in Appendix IID. 40. The chemically activated adduct $[C(OO.)H_2OH]^*$ has enough energy to go to CH_2O + HO_2, HCO_2H + OH and HC(OOH)=O + H product channels via two hydroperoxide isomers $C(OOH)H_2O.$ and C.(OOH)HOH. The HC(OOH)=O will undergoes β-scission to HC(O.)=O + OH, and the HC(O.)=O radical soon go to carbon monoxide by releasing OH radical and carbon dioxide by losing H atom (see Appendix IID. 42-43). The HCO_2H decay via C.(OH)=O and HC(O.)=O radical by abstraction reaction, or directly decompose to CO + H_2O and CO_2 + H_2 at high temperatures (see Appendix IID. 44).

Formaldehyde, important intermediate from oxidation of iso-butene and methanol, decays mostly by abstraction reactions of H, O, OH, and CH_3 radicals or atoms to CHO radical, which easily decomposes to carbon monoxide or is converted through reaction with O_2 to final products CO + HO_2 and CO_2 + OH (see Appendix IID. 41). The direct dissociation of CH_2O to CO + H_2 can also be important at high temperatures. The barrier for CH_2O → CO + H_2 is ca 35.3 kcal-mol^{-1} based on the NIST fit value (Appendix IID. 45).

8.4.4 Reactions of CH_4, C2 and C3

Methane, ethylene and propene are observed as important products from MTBE oxidation and pyrolysis at intermediate temperatures. The reaction system are described below, the potential energy level diagrams and the high pressure limit input parameters for QRRK calculations are documented in Appendix IID. 46 - 86.

The initial intermediate radical from methane decay is methyl radical, which can be formed from abstraction reactions of methane by H, O, OH and CH_3. The methyl radical can react with O_2 to go to formaldehyde (Appendix IID. 47) or CH_3O + O and therefore go to the final product CO and CO_2.

The most important C2 product from MTBE oxidation and pyrolysis is ethylene (C_2H_4), which can also be formed from methyl radical recombination and ethyl radical reacting with O_2. The potential energy level diagrams in Appendix IID. 49-52 show that the OH or HO_2 radical addition to ethylene followed by O_2 additions can convert C_2H_4 to CH_3CHO, CH_2O, C=COH, C=COOH and C(OOH)CHO, which can undergo further abstraction, β-scission reactions to final products CO and CO_2. The other important reaction pathways included in this study for C2 species are C_2H_5 + O_2, C_2H_3 + O_2, and C_2H_2 + O_2, the products from these reactions are C_2H_4, CH_3CHO, CHOCHO, CH_2O, CO, C=C=O, CHO, HO_2, OH, CH_3, and H. The potential energy level diagrams are in Appendix IID. 59-63. The abstraction and dissociation reactions of dimethylether (COC) and O_2 addition to COC. radical are included and potential energy level diagrams are in Appendix IID. 64-66. The decay of COC is via dissociation to the COC. radical or O_2 addition to COC. radical to go to formaldehyde therefore final CO and CO_2. The potential energy level diagrams and QRRK input parameters are detailed in Appendix IID. 49 - 66.

The reactions of C3 species are focused on (1) CC.C + O_2 → CC=C, CCyCOC, C2C=O and HO_2, OH radicals (Appendix IID. 67); (2) C=CC. + O_2 → C=CC=O, CH_2O, CyCOC, C.CHO, $CH_3C.=O$, CC.OH, OH (Appendix IID. 68); (3) C=CC + HO_2/OH, O_2 → CCyCOC, CC(OOH)CHO, CC(OH)CHO, CyCOC(C)OOH, CyCOC(C)OOH,

CC(=O)COOH, CC(=O)COH, CH_3CHO, C2C=O, C=C(OH)C, C=CCOOH, CC=COOH, C=CCOH, CC=COH, C=COH, CCCHO, CH_2O, CC.OOH, C_2H_5, CH_2OH, CH_3, OH, HO_2, H. The potential energy level diagrams for (3) are in Appendix IID. 70-77, and relative intermediate reactions are illustrated in Appendix IID. 78-86.

8.5 Conclusion

Chemical activation and unimolecular dissociation reactions in MTBE oxidation and pyrolysis system have been analyzed with QRRK calculations incorporated pressure dependence. The initial reactions of MTBE in the presence of O_2 are unimolecular dissociation and abstraction reactions while OH, O, HO_2 and CH_3 are the most important radicals, and initial thermal decomposition of MTBE becomes more important with increasing temperature. The major products from initial oxidation of MTBE are iso-butene, methanol, acetone, propene and formaldehyde. The most important pathways in the MTBE oxidation are (1) unimolecular dissociation of MTBE to iso-butene and methanol, (2) abstraction reactions between MTBE and H, CH_3, OH, O_2 radicals, and between CH_2O and HO_2, (3) dissociation of formaldehyde, (4) further oxidation of iso-butene via C2C=C + OH/HO_2 → intermediates, intermediates + O_2, and (5) further oxidation of methanol via CH_3OH → CH_2OH (abstraction), $CH_2OH + O_2$, and (6) further oxidation of formaldehyde via CH_2O → CHO (abstraction), $CHO + O_2$. The secondary important products from further oxidation of major products are C2C=C, C2C=O, CH_2O, CH_4, C_2H_4, C_3H_6, C2CyCOC, C=C(C)CHO, C2C=C=O, C=C(C)COH, C2CCOH, CO and CO_2.

The initial step in MTBE pyrolysis is thermal dissociation of MTBE. The thermal decomposition of CH_2O and abstraction and addition reactions are responsible for the concentration level of CH_2O. The H atom and CH_3 radical plays key role in all abstraction reactions after MTBE dissociation, while the most important products are almost the same as those from MTBE oxidation with no CO_2 and more CH_4. The formaldehyde and iso-butene are more stable at the low temperatures in the pyrolysis situation.

CHAPTER 9

MODEL VALIDATION FOR MTBE SYSTEM

9. 1 Available Literature Data

Few literature data are available for validation of MTBE model on pyrolysis and oxidation. Previous studies on MTBE pyrolysis focused on MTBE unimolecular dissociation reaction C3COC → C2C=C + CH_3OH, the rate constant we used in this study is compared to literature data as below.

	k (s^{-1}) (E_a in kcal-mol^{-1})	$k_{600\,K}$ (s^{-1})	$k_{800\,K}$ (s^{-1})	$k_{1000\,K}$ (s^{-1})
Daly [84]	$10^{14.38}$exp(-61.54 /RT)	9.0×10^{-9}	3.69×10^{-3}	8.50×10^{0}
Choo [85]	$10^{13.9}$exp((-59.0±1.0)/RT)	2.5×10^{-8}	6.03×10^{-3}	1.01×10^{1}
Brocard [86]	$10^{14.0}$exp(-59.6 /RT)	1.9×10^{-8}	5.21×10^{-3}	9.40×10^{0}
Average	$10^{14.03}$exp(-60.05 /RT)	1.77×10^{-8}	4.98×10^{-3}	9.33×10^{0}
This study	$10^{10.34}$ $T^{1.22}$exp(-59.54 /RT)	1.00×10^{-8}	4.12×10^{-3}	9.69×10^{0}

The second focus of previous study on MTBE was abstraction reactions of MTBE by OH radical. The overall rate constants reported are 1.51×10^{-12} cm^3-$molecule^{-1}s^{-1}$ by Cox et al [87]; $(5.1 \pm 1.6) \times 10^{-12}$exp[(-(155±100)/T] cm^3-$molecule^{-1}s^{-1}$ by Wallington et al [88]; (3.24±0.08) × 10^{-12} cm^3-$molecule^{-1}s^{-1}$ by Wallington et al [89]; (2.99±0.12) × 10^{-12} cm^3-$molecule^{-1}s^{-1}$ by Smith et al [91], and our rate constants are $10^{7.03}$ $T^{2.0}$exp(-0.525 kcal-mol^{-1} /RT) cm^3-$mol^{-1}s^{-1}$ for C3COC + OH → C3.COC + H_2O ($k_{600\,K}$ = 4.16×10^{-12} cm^3-$molecule^{-1}s^{-1}$; $k_{800\,K}$ = 8.25×10^{-12} cm^3-$molecule^{-1}s^{-1}$; $k_{1000\,K}$ = 1.38×10^{-11} cm^3-$molecule^{-1}s^{-1}$) and $10^{12.8}$ T^{0}exp(-0.739 kcal-mol^{-1} /RT) cm^3-$mol^{-1}s^{-1}$ for C3COC + OH → C3COC. + H_2O ($k_{600\,K}$ = 5.60×10^{-12} cm^3-$molecule^{-1}s^{-1}$; $k_{800\,K}$ = 6.54×10^{-12} cm^3-$molecule^{-1}s^{-1}$; $k_{1000\,K}$ = 7.18×10^{-12} cm^3-$molecule^{-1}s^{-1}$).

Early investigations on product distribution of MTBE oxidation were conducted by Tuazon et al [90] and Smith et al [91] in the presence of NOx (see chapter 6). Dunphy and Simmie's[92] studied on the oxidation of MTBE but did not report any product distributions except ignition delay times verse temperatures.

Only available literature data in our knowledge are from Norton et al [93] and Held et al [94]. Please see discussion in section 9.3.

9.2 Comparison With Experimental Data at 4, 7 and 10 Atm

The modified CHEMKIN [83] computer code, which employs Chebyshev polynomials (7 × 3) to incorporate the pressure and temperature dependence (0.001 to 100 atm, 200 to 2500 K) into rate constant expressions, is used to integrate the kinetic equations and to calculate reverse rate constants from the forward rate constants and thermodynamic parameters. The pressure and temperature combined mechanism includes 1265 reactions and 268 species.

As shown in previous chapters, important products of MTBE decay under either pyrolysis or oxidation conditions are C2C=C, CH_3OH, C2C=O, C_3H_6, C_2H_4, CH_4, C=C(C)CHO, CO and CO_2. In current stage, model calculations agree with experimental results under some conditions and predict the trend of product distribution.

Comparisons of model calculations, on the time dependence of the reactant (MTBE) decay and major products (C2C=C, CH_3OH, CH_4, C2C=O and C_3H_6) formation, to experimental data collected in this study under the pyrolysis and oxidation conditions are illustrated in Appendix IIC Figure 125 - 148.

9.2.1 Fuel Lean Mixture

A comparison of experimental results and model calculations for fuel lean mixtures at different temperatures and pressures are shown in Appendix Figure IIC. 125 - 130. At pressure of 4 atm and 873 K (see Appendix Figure IIC. 125), the model predicts a slower MTBE decay than experimental data. Model calculations for C2C=C, C2C=O and CH_4 agree well with experimental results, while production of C_3H_6, CH_3OH and CH_2O from model calculations are higher than experimental results. Over-production of C_3H_6, CH_3OH and CH_2O from model along with slower MTBE decay indicate a slower reaction proceeding, which may be due to a wall effect that is not considered in the model. A difference between C2C=C and CH_3OH concentration level is shown from model but it is smaller than that from experiment. When temperature increases to 923 K, experimental data shows that MTBE quickly decays and no those major products observed or detected under the experiment conditions in 0.5 - 1.0 sec (see Appendix Figure IIC. 126). When pressure increases to 7 atm and 10 atm from 4 atm (Appendix Figure IIC. 128, Figure IIC. 129), at 873 K, similar product distributions are predicted by model calculations. Better agreement on MTBE decay and CH_4 formation, as well as CH_2O and C_3H_6 formation at 7 atm and 823 K is shown Appendix Figure IIC. 127. A trend of product distribution is predicted from model at 10 atm and 798 K. At relatively lower temperatures and higher pressures, model gives better agreement for MTBE decay and CH_4 formation while only a trend could be predicted from model for other products C2C=C and CH_3OH as well as CH_2O, C_3H_6 and C2C=O formation (Appendix Figure IIC. 127, Figure IIC. 129).

9.2.2 Chemical Stoichiometric Fuel

A better agreement between experiment and model calculation for reactant decay and product formations is obtained at 873 K and 4 atm in the stoichiometric fuel environment (Appendix IIC Figure IIC. 131). Experiment data shows that major products C2C=C and CH_3OH reach maximum levels at the early reaction stage, then start to decrease at 0.9 sec, and other products C2C=O, C_3H_6, CH_4, CH_2O increase with the reaction proceeding (0.5 - 1.2 sec). The difference between C2C=C and CH_3OH concentration levels from model calculation is smaller than that from experimental results. C2C=O and CH_4 are predicted well by model calculations, while model gives higher productions of C_3H_6 and CH_2O than that from experiments. Sensitivity analysis shows that at these conditions (873 K, 4 atm, 0.5 - 1.2 sec), MTBE decay and product formation are controlled by decomposition and oxidation of MTBE, and abstraction reactions of MTBE by radical pools, as well as further reactions of intermediate radicals and molecules. MTBE thermal decomposition, abstraction reaction of MTBE by O_2, abstraction reaction of CH_2O by HO_2 are important pathways and reactions for controlling the overall rate of reaction system and product distribution under 4 atm and 873 K. Chemical activation pathways C3C. + $CH_3O \rightarrow$ $[C3COC]^* \rightarrow$ products and C3CO. + $CH_3 \rightarrow [C3COC]^* \rightarrow$ products have important effects on product distribution, this is because chemically activated transition adducts contain more energy than thermally activated adducts do. At 873 K, experimental data become more disperse at 7 and 10 atm, which suggests a more sensitive experimental conditions. Good matches on MTBE decay and CH_4 formation between model calculation and experiment are obtained at 7 atm, 873 K, and become worse at 10 atm, 873 K. At 873 K, model calculations only predict product distribution trends but much

higher concentration levels for C2C=O, C_3H_6 at both 7 and 10 atm, for C2C=C, CH_3OH, CH_2O, model predicts down trends with residence time (1.0 - 5.6 sec) while experimental data show an up - top - down trend. At higher temperature (1023 K), model calculations seem to be differ from with experimental data, this suggest that more complex reaction pathways are involved in the reaction process. At 1023 K, few products are observed from experiment which should be accounted for by faster conversion of those products to final CO and CO_2.

9.2.3 Fuel Rich Mixture

Because of reduced O_2 concentration in the fuel mixture, both experimental data and modeling results show that more CH_4 is produced from MTBE decay. Similar predictions by model to that in stoichiometric fuel mixtures are shown in Appendix Figure IIC. 137 - 142. Model gives good fit to experimental data at 873 K and 4 atm, and under predict CH_4 at 7atm and 10 atm for both lower and higher temperatures. Model predictions on CH_3OH, C_3H_6, C2C=O, and CH_2O are higher than those from experiment at 7 atm and have better fits to experimental data at 10 atm. Under prediction on C2C=C is the case for both 7 and 10 atm at 873 K. When temperature increases, a difference occurs between model and experiments just like the case in the stoichiometric fuel environments.

9.2.4 MTBE Pyrolysis

Comparisons of model calculations to experiment data are shown in Appendix Figure IIC. 143 - 148. Good agreements for MTBE decay and major products C2C=C and CH_3OH as well as C2C=O, CH_2O and C_3H_6 formations between model calculation and

experimental data at 873 K and 4 atm are shown in Figure IIC. 143. Sensitivity analysis shows that under relatively low temperature (873 K) and pyrolysis condition only thermal decomposition of MTBE, and abstraction between MTBE and H, CH_3 radicals are important to MTBE decay. A deviation of model calculations from experiment data at 873 K and 4 atm is that more iso-butene is produced than CH_3OH from experiment while model predicts almost the same quantities of both C2C=C and CH_3OH. Also modeling result gives a little bit higher C_3H_6 production. When temperature goes to 1023 K at 4 atm, fits are seen on MTBE decay and major product C2C=C, CH_3OH formations but not on other products formation. Figure IIC. 144 (4atm and 1023 K) in Appendix IIC shows that modeling results are agree well with the experimental results for MTBE decay and C2C=C formation, CH_3OH production is a little bit lower than C2C=C in the model in contrast to a little higher CH_3OH than C2C=C at 873 K. The productions of CH_4, C2C=O, C_3H_6, and CH_2O are much lower in the model than that from experiment. In the pyrolysis environment, thermal decomposition reactions play uniquely important roles at intermediate and high temperatures, C2C=C and CH_3OH are mainly from MTBE decomposition by a four-center elimination mechanism in the almost equal amount. The chemical activation channel C3C. + $CH_3O \rightarrow [C3COC]^* \rightarrow$ products and C3CO. + $CH_3 \rightarrow [C3COC]^* \rightarrow$ products are important to CH_4 and C_3H_6 as well as C2C=O levels at 1023 K in MTBE pyrolysis system. Lower C2C=O, C_3H_6 and CH_4 levels are predicted from model calculations than that are observed, this may be accounted for by assignments of rate constants of abstraction reactions of MTBE by H, CH_3 radicals. The other major source responsible for C2C=O, C_3H_6 and CH_4 productions are the dissociation of intermediate radicals which are from MTBE thermal decomposition, sensitivity analysis

show that these intermediate's decomposition affect little on the C2C=O, C_3H_6 and CH_4 production. At 873 K, thermal decomposition of CH_2O, abstraction reactions of CH_2O by H, CH_3 radicals are responsible for concentration levels of CH_2O from MTBE decay. At 1023 K, much lower levels of formaldehyde (CH_2O) may have a little bit more complicated reasons since CH_2O can be formed from many ways.

At 873 K, when pressure goes up to 7 atm and 10 atm (Appendix Figure IIC. 145, Figure IIC. 147), much faster decay of MTBE, a little bit higher level of CH_3OH, and higher level of C_3H_6, lower levels of C2C=O and CH_2O, are observed in the model.

At 1023 K, when pressure goes higher, the discrepancies of model calculations from experimental results become larger for CH_4 and C2C=O, smaller for C_3H_6, and no change for CH_2O. Sensitivity analysis shows that the under predictions by model is due to lower productions of these species and is not due to dissociation of these species, nor by abstraction consuming of produced species. So, one of the reasons responsible for these discrepancies may be that we missed some other reaction pathways.

9.3 Comparison to Experimental Data at 1 Atm

Model calculations are also compared to experimental data at 1 atm. Experimental data at 1 atm, 923 K, and in both pyrolysis and stoichiometric oxidation environments were taken from this laboratory's previous work, and experimental data at 1 atm, 1028 K in oxidation (φ = 0.96) environment were taken from Princeton's work, Held et al [94]. The comparisons with these experimental data at 1 atm are shown in Appendix Figure IIC. 49 - 51. The better fit is obtained at the condition of 1 atm, 923 K and stoichiometric oxidation environment. Faster decay of MTBE along with higher levels of C2C=C and

CH_3OH are observed in the model for experimental data at the conditions of 1 atm, 923 K and pyrolysis. Finally, model predicts much higher levels of C2C=C and CH_3OH, and much lower levels of CH_4, C_2H_6, C3H4, C_3H_6, C2C=O and CO for the experimental data under the conditions of 1 atm, 1028 K and oxidation (φ = 0.96).

PART IV

TRANSITION STATES FOR R1R2C.CCOOH → R1R2C=C + C.H_2OOH

CHAPTER 10

STUDY ON R1R2C.CCOOH → R1R2C=C + C.H$_2$OOH

10.1 Overview

One interest and thrill of physical chemistry lies not so much in what reactants turn into which products but in the intricacies of the journey from one to the other- a journey that almost always involves a transition state, the heart of a chemical reaction.

A specific reaction series: one of beta scission of C.CR'COOH, hydroperoxy alkyl radical to form an olefin plus a hydroperoxy methyl radical RC.OOH. This RC.OOH radical rapidly decomposes to lower energy products: RCHO + OH. Little or no evidence is observed for formation of the final products in the transition state of the first beta scission step. The primary alkyl radical is represented as RC., where R is alkyl group with at least one C (alkyl group such as CH_3 or C_2H_5) attached. It can be represented as (R1R2C)C (R1 and R2 are either alkyl groups or H). RC. reacts with O_2 to form peroxide radical (R1R2C)CCOO. because of the high relative concentration of O_2 in combustion and that the reaction occurs with no energy of activation, and further undergoes isomerization reaction to form hydroperoxide radical (R1R2C).C-CH_2OOH: C3.CCOOH (R1 = R2 = CH_3), C2.CCOOH (R1 = CH_3, R2 = H), and C.CCOOH (R1 = R2 = H). β-scission occurs to release C.R1R2OOH radical and form an alkene species. The peroxide radical (R1R2C)CCOO. can also form (R1R2C)CC.HOOH (RC.HOOH) radical. Note here and in all cases where a C.H_2OOH or a R-C.HOOH is formed; this type carbon radical when centered adjacent to a peroxy group will rapidly decompose to CH_2O + OH or RCHO + OH as the reaction is ca 30 kcal mole^{-1} exothermic and has little or no barrier ([96] Page,

1990). The geometric structure of C.H_2OOH radical, please see, as shown in figure in Appendix TS III. 5, calculated by MOPAC PM3 also indicates that it is a very unstable radical. The CH_2O--OH bond has a 1.93 Å of bond length in the individual molecule which is much longer than normal O--O bond and in breaking status, the CH_2--OOH bond, on the contrary, has a 1.207 Å of bond length which is very close to normal bond length in CH_2O (1.202 Å).

One of the concerns is the rate constant for C.H_2OOH elimination reactions and the other one is whether there are two steps for hydroperoxide alkyl radical go to final products alkene + CH_2O + OH. or, is the entire reaction process the one step where the transition state sees the intermediate. The rate constants for C.H_2OOH radical elimination reactions are usually estimated from reverse addition reaction, and the addition reaction of CH_3 radical to ethylene (C=C) has been taken as reference reaction since no literature data for C.H_2OOH radical addition to alkene is available. Knowing the steps for a hydroperoxide alkyl radical to go to final products CH_2O + OH + alkene is important for understanding this C.H_2OOH elimination or RC.HOOH formation reactions.

In this study, we calculate three transition states which are the first examples of such a system where a C.H_2OOH or a R-C.HOOH is formed, using semi-empirical (MOPAC PM3) method. Transition state theory and thermodynamic analysis are employed to obtain A factors for reactions. Thermodynamic properties of transition states and related species are listed in Appendix 3 TS III. 1. The bond lengths in reactants, transition states and products are listed in Appendix 3 along thermodynamic analysis information thus A factors.

10.2 C.CCOOH → C=C + C.H$_2$OOH

Transition state for reaction C.CCOOH → C=C + C.H$_2$OOH has been found and shown in Appendix TS III. 1. We notice that three bond lengths suffer large change between reactant, transition state and products. The forming carbon double bond, which has one carbon with radical site on and another carbon with C.H$_2$OOH radical on, has a 1.462 Å of bond length in reactant (C.CCOOH), a 1.347 Å of bond length in transition state and a 1.322 Å of bond length as a typical double bond in alkene (C=C). The breaking bond CC - COOH has a normal bond length of 1.530 Å in reactant (C.CCOOH), a 2.096 Å bond length is observed in the transition state. The much longer bond length in transition state of this breaking bond combining the bond length of the forming double bond which is very close to a typical double bond length indicates that the transition state is ready for forming products, a 2.80 × 10^{13} of A factor at 800 K is obtained from the calculation employing transition state theory based on $\Delta S^{\neq}$ from thermodynamic analysis for reaction C.CCOOH → TS. With the increasing temperature, $\Delta S^{\neq}$ increases quickly from 8.45 × 10^{-16} at 300 K to 3.34 × 10^{-3} at 2000 K, which indicates increasing A factor therefore rate of reaction.

10.3 C2.CCOOH → CC=C + C.H$_2$OOH

Transition state for reaction C2.CCOOH → CC=C + C.H$_2$OOH is shown in Appendix TS III. 2. In transition state we found similar bond lengths to that for reaction C.CCOOH → C=C + C.H$_2$OOH. The forming double bond has its bond length change from 1.471 Å in reactant to 1.357 Å in transition state, and 1.328 Å in final propene (CC=C). The breaking C2.C-COOH bond has its bond length change from 1.540 Å in the reactant to 2.090 Å in the transition state. The A factor of 3.48 × 10^{13} at 800 K is calculated the

same way as that for reaction C.CCOOH → C=C + C.H_2OOH, and is a little bit larger than that of reaction C.CCOOH → C=C + C.H_2OOH (2.80 × 10^{13} at 800 K). A increasing $\Delta S^{\neq}$ with temperature, thus an increasing A factor, a positive temperature dependence of rate constant is found for this reaction.

10.4 C3.CCOOH → C2C=C + C.H_2OOH

Calculation for C3.CCOOH → C2C=C + C.H_2OOH shows consistent data with the above (C.CCOOH, C2.CCOOH) two reactions. The forming carbon double bond change its bond length from 1.488 Å in the reactant to 1.364 Å in the transition state, and to 1.334 Å as a typical carbon double bond in iso-butene, and the breaking C3.C - COOH bond has a 2.096 Å bond length in the transition state while a 1.548 Å in the reactant radical C3.CCOOH (Appendix TS III. 3). The bond lengths in the transition state well consistent with that in the above two reaction transition states (Appendix TS III. 5). A positive temperature dependence of rate constants is seen from increasing $\Delta S^{\neq}$ with temperature via thermal reaction analysis (Appendix TS III. 9).

The other interesting bond lengths in the three transition states is RC--OOH bond and RCO--OH bond. We notice that the three transition states have almost the same RC--OOH bond length of 1.345 Å, which are a little bit shorter than that in the reactants (1.411 Å, 1.412 Å and 1.394 Å for C.CCOOH, C2.CCOOH and C3.CCOOH respectively), much longer than a C=O double bond in CH_2O (1.202 Å). Almost the same bond lengths of 1.534 Å are found in the three transition states for RCO--OH bond, which is longer than a typical O--O bond length (1.40 Å). But we do not see a trend of final products CH_2O + OH being formed at the same time of beta scission.

At this point, we also conclude that the MOPAC PM3 calculation does not show any change in the bond length in the transition states when the substitutes on the carbon connected to both C.H_2OOH and radical site (carbon) change from two H to two methyl groups. This indicates a similar A factor could be used for this type reactions.

10.5 C.$H_2OOH \rightarrow CH_2O + OH$

Comparing bond lengths of RC--OOH and RCO--OH in the transition states to that in the reactants (see discussion above), we do not see any evidence of the one step process for hydroperoxy alkyl radical to go directly to final product alkene + CH_2O + OH. The C=O bond length in CH_2O is 1.202 Å, the C.H_2OOH radical (Appendix III. 1-4) has a bond length of 1.930 Å for CO--OH bond and a bond length of 1.207 Å for C--OOH bond, this indicates the CH_2O + OH must be rapidly formed after formation of C.H_2OOH. Appendix III. 4 shows MOPAC calculation information for reactant and products of reaction C.$H_2OOH \rightarrow CH_2O$ + OH, we did not find transition state for this reaction. Thermodynamic analysis was performed for this reaction (Appendix III. 10) and the temperature dependence of reaction thermodynamic properties are small. And we may conclude here again that there are two steps instead of one step for hydroperoxide alkyl radical to go to the final products CH_2O + OH + alkene, and the first step is rate controlling step.

10.6 Thermodynamic Analysis and QRRK Analysis

One of the reason for us to concern this specific type of beta scission – C.H_2OOH elimination reactions, was to obtain the rate constants because they are important

reactions in combustion conditions: high O_2 level and the following dissociation of $C.H_2OOH$ radical occurs with no energy of activation as we discussed above.

Thermodynamic properties of related reactants, transition states and products were calculated using MOPAC PM3 method and listed in Appendix III. 6. Thermodynamic analysis performed for three reactions are shown in Appendix TS III. 7-9. The A factor is calculated by use of transition state structures and the fit value in the temperature range 300 K to 2000 K is used as high pressure limit parameter for QRRK calculation. The activation energy is estimated in usual way as we mentioned in chapter 2 for β-scission reaction. A 7.8 kcal-mol^{-1} of $E_{a,r}$ is used for reverse addition reaction of the $C.H_2OOH$ to the alkene double bond. The $E_{a,f}$ for β-scission reaction can then be calculated using the principle of microscopic reversibility ($E_{a,f} = E_{a,r} + \Delta U_{rxn}$). The potential energy level diagram in Appendix TS III.11 shows a small decrease on $E_{a,f}$ for dissociation of C.CCOOH, C2.CCOOH and C3.CCOOH respectively. This is due to the decrease on ΔU_{rxn}. The ΔU_{rxn} avg. (298, 1500 K) of dissociation reaction of C.CCOOH, C2.CCOOH and C3.CCOOH are 22.03, 20.77 and 19.56 kcal-mol^{-1} respectively, and the calculated $E_{a,f}$ are 29.8, 28.57 and 27.36 kcal-mol^{-1}. The temperature dependence of rate constants of these three reactions shown in Appendix TS III.12 illustrate a similar trend for three reactions. A slightly higher rate constant is observed for the higher substituted hydroperoxide radicals ($k_{C3.CCOOH} > k_{C2.CCOOH} > k_{C.CCOOH}$).

Appendix TS III.13-14 shows the pressure dependence of rate constants of three reactions. At 700 K, the high pressure limit rate constant (k_∞) is observed at about 1 atm for reaction C.CCOOH → TS → C=C + $C.H_2OOH$ and C2.CCOOH → TS → CC=C +

$C.H_2OOH$, 10 atm for reaction C3.CCOOH → TS → C2C=C + $C.H_2OOH$. At higher temperature (1100 K), the pressure dependence of rate constants is observed in a wide pressure range for all three reactions (k_∞ is not observed even at 100 atm), which indicates the pressure dependence of rate constant becomes much more important under the higher temperature conditions such as combustion. Appendix TS III.13-14 also show that the higher substitute (C3.CCOOH), the larger dependence of rate constant on pressure.

One other interesting trend for this type of reaction is the estimation of activation energy directly from MOPAC calculations. The heat of formations for three radicals and three alkene from THERM (group additivity) and MOPAC calculations (including corrections) are illustrated in Appendix TS III. 15 along with the activation energies from two methods (MOPAC and thermo chemical kinetics). We see a linear trend in the three sets of data, and a certain percent of overestimation for E_a. In this case, 16-18% of overestimation for E_a is found. Also we notice the lower heat of formation the hydroperoxide alkyl radical has, the lower ΔU_{rxn} thus lower E_a whether the E_a is from THERM or MOPAC, and the less overestimation for E_a. This suggest that direct estimation of E_a from MOPAC may be possible after more reactions are analyzed in order to get a more accurate value of percent of overestimation. But higher level of calculation such as Gaussian 94 (MP2) or density function are needed to verify MOPAC results.

10.7 Conclusion

Three examples for $C.H_2OOH$ elimination reactions are analyzed in this study. Transition states, thermodynamic properties, A factors are calculated from MOPAC PM3 method. QRRK analysis is performed and shows a similar trend in the temperature and pressure

dependence of rate constants. Analysis also shows that MOPAC calculation for heat of formation of species could also be able to used with consideration of over- or under-estimations, therefore E_a can be directly obtained from MOPAC calculations. More analysis on this type of reactions need to be done.

APPENDIX IA

TABLES IN THE NEO-C_5H_{11} + O_2 SYSTEM

Table IA. 1 Thermodynamic Properties for Species in the Neo-C_5H_{11} + O_2 System

SPECIES	H_{f298}	S_{298}	Cp							
			300	400	500	600	800	1000	1500	
HE	0.00	30.12	4.97	4.97	4.97	4.97	4.97	4.97	4.97	a
O_2	0.00	49.00	6.86	7.10	7.33	7.54	7.89	8.18	8.70	a
H	52.10	27.30	4.90	4.90	4.90	4.90	4.90	4.90	4.90	a
OH	9.50	43.80	6.79	6.86	6.93	7.00	7.14	7.28		a
CH_3	34.80	46.30	9.12	9.91	10.68	11.41	12.75	13.9	16	a
C_2H_6	-20.40	55.08	12.38	15.68	18.80	21.58	26.04	29.54	35.16	c
I	25.50	43.20	5.00	5.00	5.00	5.00	5.00	5.00	5.00	b
C2C(COOH)COO.	-46.58	114.55	43.74	52.59	60.17	67.15	76.37	83.75		c
C2.C(COOH)COOH	-33.68	119.55	45.20	54.11	61.67	68.59	77.59	84.66		c
C=C(C)COOH	-24.38	90.10	30.23	36.16	41.22	45.79	52.26	57.51		c
C=C(C)CO.	13.70	80.55	23.83	28.87	33.43	37.38	43.75	48.41	55.38	c
C2C(COOH)C=O	-79.49	103.12	37.92	46.40	53.83	60.29	69.30	75.91		c
C2C(CO.)C=O	-42.14	94.04	31.71	39.64	46.56	52.29	60.91	66.84		c
C=C(C)C=O	-27.34	74.64	23.14	28.34	32.66	36.17	41.73	45.56		c
C2C=O	-51.56	70.09	17.97	22.00	25.89	29.34	34.93	39.15		c
CH_2O	-26.00	50.92	8.47	9.38	10.46	11.52	13.37	14.81		c
CH3O	3.96	55.84	9.51	11.04	12.61	14.13	16.67	18.58	21.43	c
C3.COH	-26.10	85.40	26.61	32.89	38.22	42.65	49.78	55.10		c
C2C(OH)COO.	-60.19	98.67	33.48	40.34	46.10	51.19	58.68	64.63		c
C2C(O.)COOH	-44.33	96.99	34.55	41.88	48.04	53.39	61.02	66.80		c
C2C.COH	-24.10	88.49	25.43	30.55	35.54	40.14	47.73	53.51		c
C2C(OO.)COH	-59.38	97.27	33.38	40.26	45.97	51.04	58.32	64.16		c
C2C(OOH)CO.	-43.52	95.59	34.45	41.80	47.91	53.24	60.66	66.33		c
C2C.OOH	-8.48	87.31	26.55	30.69	34.50	38.21	43.48	47.93		c
CH_2OOH	14.60	68.25	16.55	18.40	19.87	21.44	23.20	24.93		c
CH_3OO	4.30	65.18	13.88	15.47	16.85	18.44	20.49	22.71		c
C2CyCCOC	-33.33	77.34	26.78	35.56	43.27	49.57	58.91	65.50	75.54	d
C4C	-40.30	72.87	29.13	37.49	44.96	51.28	60.85	67.84	78.44	c
C3CC.	8.70	80.84	28.54	36.17	42.91	48.63	57.35	63.78	73.57	c
C3CCOO.	-25.39	93.62	34.19	42.97	50.69	57.01	66.47	73.23	83.65	d
C3.CCOOH	-12.49	101.74	36.32	45.45	53.22	59.42	68.32	74.46	83.82	d
C3CC.OOH	-17.59	97.71	37.60	45.62	52.68	58.96	67.79	74.49		c
C2C=C	-3.80	69.99	21.58	26.65	31.30	35.34	41.91	46.89	54.71	c
C=C(C)COOH	-24.38	90.10	30.23	36.16	41.22	45.79	52.26	57.51		c
C3CC=O	-58.30	82.68	29.59	37.43	44.45	50.31	59.18	65.47		c
C2C=C=O	-28.06	73.97	24.08	28.58	33.01	36.14	41.27	45.33	51.36	c
C3CCI	-22.10	90.40	32.14	40.65	48.46	54.39	63.63	70.27		c

Table IA. 1 Thermodynamic Properties for Species in the Neo-C_5H_{11} + O_2 System (Cont')

SPECIES	H_{f298}	S_{298}	Cp							
			300	400	500	600	800	1000	1500	
C3.CCI	26.90	97.79	31.55	39.33	46.41	51.74	60.13	66.21		c
C3CC.I	26.90	93.43	31.55	39.33	46.41	51.74	60.13	66.21		c

a. *JANAF Thermochemical Tables* 3rd ed. NSRDS-NBS, 37, 1986.
b. Benson, S. W. *Thermochemical Kinetics* 2nd ed. Wiley, New York, 1976.
c. THERM: Computer Code for Thermodynamic Properties Estimation Ritter, E. R., Bozzelli, J. W. *Intl. J. Chem. kinet.* 23, 767, 1991.
d. H_{f298} are from THERM, S^{298} and $C_p(T)$ is sourced from MOPAC PM3 calculations.

Table IA. 2 Comparison of Current Rates with Literature Recommendations

Sources	High Pressure limit parameters	Rate Constant [h]
Unimolecular Dissociation of Neopentyl: C3CC . → C2C=C + CH_3		
Hughes[a]	$k(s^{-1}) = 10^{13.9\pm0.5} \exp(-30.90 \pm 1.0 \text{ kcal-mol}^{-1}/RT)$[d]	1.49×10^{4}
Baldwin[b]	$k(s^{-1}) = 10^{13.65\pm0.2} \exp(-30.48 \pm 1.44 \text{ kcal-mol}^{-1}/RT)$	1.36×10^{4}
Curran[c]	$k(s^{-1}) = 10^{13.98} \exp(-30.90 \text{ kcal-mol}^{-1}/RT)$	8.92×10^{3}
NJIT	$k(s^{-1}) = 10^{13.90} \exp(-30.76 \text{ kcal-mol}^{-1}/RT)$[e]	1.09×10^{4} [i]
Isomerization of Neopentyl: C3CCOO. → C3.CCOOH		
Hughes	$k(s^{-1}) = 10^{12.2} \exp(-29.4 \text{ kcal-mol}^{-1}/RT)$	1.23×10^{3} [j]
Baldwin	$k(s^{-1}) = 10^{13.08} \exp(-28.7 \text{ kcal-mol}^{-1}/RT)$	1.31×10^{4}
Curran	$k(s^{-1}) = 10^{12.35} \exp(-23.9 \text{ kcal-mol}^{-1}/RT)$	7.66×10^{4}
NJIT	$k(s^{-1}) = 10^{9.7} T^{1.0} \exp(-22.7 \text{ kcal-mol}^{-1}/RT)$[f]	1.15×10^{5} (forward) 1.10×10^{7} (reverse) [i]
Epoxide Formation from Neopentyl Hydroperoxide: C3.CCOOH → C2CyCCOC + OH		
Hughes		
Baldwin	$k(s^{-1}) = 10^{11.30} \exp(-17.46 \text{ kcal-mol}^{-1}/RT)$	7.05×10^{5}
Curran	$k(s^{-1}) = 10^{10.40} \exp(-15.25 \text{ kcal-mol}^{-1}/RT)$	4.33×10^{5}
NJIT	$k(s^{-1}) = 10^{7.7} T^{0.71} \exp(-14.0 \text{ kcal-mol}^{-1}/RT)$[f]	9.77×10^{4} [i]
Dissociation of Neopentyl Hydroperoxide: C3.CCOOH → C2C=C + CH_2OOH		
Hughes		
Baldwin	$k(s^{-1}) = 10^{13.65} \exp(-27.75 \text{ kcal-mol}^{-1}/RT)$	9.73×10^{4}
Curran	$k(s^{-1}) = 10^{13.70} \exp(-29.00 \text{ kcal-mol}^{-1}/RT)$	4.41×10^{4}
NJIT	$k(s^{-1}) = 10^{13.72} \exp(-28.18 \text{ kcal-mol}^{-1}/RT)$[g]	1.87×10^{4} [i]

(a) Hughes, Kevin J.; Halford-maw, Peter A.; Lightfoot, Phillip D.; Turanyi, Tamas and Pilling, Michael J., 24th Symposium (International) on Combustion/The Combustion Institute, 645-652 (1992)
Hughes, K. J.; Lightfoot, P. D.; and Pilling, M. J., Chemical Physics Letters, 191(6), 581-586 (1992)

(b) Baldwin, R. R.; Hisham, M. W. M. and Walker, R. W., J. Chem. Faraday Trans. I, 78, 1615-1627 (1982)

(c) Curran, H. J.; Pitz, W. J.; Westbrook, C. K.; Hisham, M. W. M. and Walker, R. W., for The 26th International Symposium on Combustion, Naples, Italy.

(d) Slagle, I. R.; Batt, L.; Gmurczyk, G. W. Gutman, D. and Tsang, W., The Journal of Physical Chemistry, 95(20), 7732-7739 (1991)

(e) Fit to Gutman's (d) experimental data for rate constant

(f) Based on TST. $\Delta S^{\circ}(T)$ was taken from semi-empirical and Ab Initio calculations. see text for detail

(g) Calculated from reverse reaction. $A_r = 10^{11.2}$ s^{-1}, $Ea_r = 7.8$ kcal $mole^{-1}$ (this work)

(h) Calculated from rate constant expression at 700 K

(i) Result from RRK calculation

(j) Experimental value from (a)

Table IA. 3 Important Reactions Responsible for the Formation of OH

Reactions[a]	Percent (%)[b]
C3CC. + O_2 => C2CyCCOC + OH	69.65
C3CC. + O_2 => C3CC=O + OH	7.39
C3.CCOOH + O_2 => C=C(C)COOH + CH_2OOH C3CC. + O_2 => C2C=C + CH_2OOH CH_3 + O_2 => CH_2O + OH	22.96

(a) Conditions: T= 700 K, P_{total} = 0.807 atm, [C5H11I] = 7 $\times 10^{12}$ cm^{-3}, $[C5H11I]_0$ = 3$\times 10^{11}$ cm^{-3} P_{O2} = 63.3 Torr, Bath gas = He

(b) data were taken at the top point of OH growth curve

Table IA. 4 The Reaction Mechanism for Neopentyl Radical + O_2

Reactions	A[a]	n	E[b]	
C3CCI <=> C3CC. + I	1.00E+16	0	52100	c
C3CCI + OH <=> C3.CCI + H_2O	6.80E+08	1.42	899.6	c
C3CCI + OH <=> C3CC.I + H_2O	1.16E+08	1.55	204.7	c
C3CC.+ O_2 <=> C3CCOO.	5.32E+45	-10.99	8972	d
C3CC.+ O_2 <=> C3.CCOOH	9.58E+38	-8.31	13555	d
C3CC.+ O_2 <=> C2C=C + CH_2OOH	4.91E+42	-8.65	27178	d
C3CC.+ O_2 <=> C2CyCCOC + OH	1.31E+41	-8.82	20996	d
C3CC.+ O_2 <=> C=C(C)COOH + CH_3	5.41E+42	-8.66	26991	d
C3CC.+ O_2 <=> C3CC.OOH	1.90E+15	-2.31	19285	d
C3CC.+ O_2 <=> C3CC=O + OH	3.80E+21	-2.92	21244	d
C3CCOO. <=> C3.CCOOH	6.07E+42	-9.81	31384	d
C3CCOO. <=> C2C=C + CH_2OOH	1.90E+61	-14.69	56786	d
C3CCOO. <=> C2CyCCOC + OH	2.56E+50	-12.01	43926	d
C3CCOO. <=> C=C(C)COOH + CH_3	1.60E+61	-14.67	56501	d
C3CCOO. <=> C3CC.OOH	1.90E+40	-10.41	51004	d
C3CCOO. <=> C3CC=O + OH	4.68E+46	-11.07	52949	d
C3.CCOOH <=> C2C=C + CH_2OOH	2.15E+29	-5.34	31508	d
C3.CCOOH <=> C2CyCCOC + OH	1.25E+19	-3.14	16575	d
C3.CCOOH <=> C=C(C)COOH + CH_3	1.70E+29	-5.32	31177	d
C3CC.OOH <=> C3.CCOOH	5.01E+17	-4.94	575	d
C3CC.OOH <=> C3CC=O + OH	1.19E+05	1.07	-1948	d
CH_2OOH <=> HCHO + OH	3.63E+10	-0.66	595	d
C3CC. <=> C2C=C+CH_3	2.04E+47	-10.85	39743	d
CH_3 + O_2 <=> CH_3OO	8.61E+31	-6.59	4931	d
CH_3 + O_2 <=> HCHO + OH	2.85E+08	1	12526	d
C3.CCOOH + O_2 <=> C2C(COOH)COO.	4.88E+39	-9	7456	d
C3.CCOOH + O_2 <=> C2.C(COOH)COOH	6.91E+38	-8.43	13957	d
C3.CCOOH + O_2 <=> C=C(C)COOH + CH_2OOH	1.16E+45	-9.38	29174	d
C3.CCOOH + O_2 <=> C2C(COOH)C=O + OH	6.01E+18	-3.24	21727	d
C2C(COOH)COO. <=> C2.C(COOH)COOH	7.59E+36	-8.18	28541	d
C2C(COOH)COO. <=> C=C(C)COOH + CH_2OOH	7.81E+56	-13.26	56447	d
C2C(COOH)COO. <=> C2C(COOH)C=O + OH	6.20E+35	-8.79	50582	d
C2.C(COOH)COOH <=> C=C(C)COOH + CH_2OOH	1.54E+26	-4.21	31584	d
C2.C(COOH)COOH <=> C2C(COOH)C=O + OH	4.00E+32	-8.05	40578	d
C=C(C)COOH <=> C=C(C)CO. + OH	2.33E+45	-9.68	53233	d
C=C(C)CO. <=> C=C(C)C=O + H	5.11E+43	-10.62	20054	d
C2C(COOH)C=O <=> C2C(CO.)CO + OH	1.45E+43	-8.92	52055	d
C2C(CO.)CO <=> C2C.C=O + HCHO	1.12E+10	-0.55	426	d
C2C.C=O <=> C=C(C)C=O + H	3.29E+29	-5.25	45282	d
C2C.C=O <=> C2C=C=O + H	7.26E+28	-5.08	44459	d
C2C=C + OH <=> C3.COH	9.34E+41	-9.52	8698	d
C3.COH + O_2 <=> C2C(OH)COO.	1.78E+47	-11.4	9255	d

Table IA. 4 The Reaction Mechanism for the Neopentyl Radical + O_2 (Cont')

Reactions	A[a]	n	E[b]	
C3.COH + O_2 <=> C2C(O.)COOH	6.30E+32	-7.74	8612	d
C3.COH + O_2 <=> C2C=O + CH_2OOH	4.71E+34	-6.98	13531	d
C2C(OH)COO. <=> C2C(O.)COOH	6.03E+44	-11.5	29831	d
C2C(OH)COO. <=> C2C=O + CH_2OOH	2.62E+55	-13.57	41747	d
C2C(O.)COOH <=> C2C=O + CH_2OOH	8.87E+29	-6.16	14484	d
C2C=C + OH <=> C2C.COH	3.38E+38	-8.4	8284	d
C2C.COH + O_2 <=> C2C(OO.)COH	1.71E+55	-14.06	11164	d
C2C.COH + O_2 <=> C2C(OOH)CO.	2.47E+37	-9.41	9477	d
C2C.COH + O_2 <=> C2C.OOH + HCHO	7.86E+37	-8.22	13561	d
C2C(OO.)COH <=> C2C(OOH)CO.	3.55E+47	-12.47	30351	d
C2C(OO.)COH <=> C2C.OOH + HCHO	2.24E+58	-14.64	41636	d
C2C(OOH)CO. <=> C2C.OOH + HCHO	8.40E+28	-5.91	13365	d
C2C.OOH <=> C2C=O + OH	1.47E+07	0.38	-1166	d
OH <=> Y	8.80E+01	0	0	e
CH_3 + CH_3 <=> C_2H_6	2.63E+65	-17.28	12709	d
$CH_3OO.$ + CH_3 <=> CH_3O + CH_3O	9.00E+12	0	0	d

a Unit is cm^3/mole-s or s^{-1}
b Unit is cal/mole
c From reference 37
d Result from QRRK calculations
e Wall loss reaction and rate constant is taken from reference 8

Table IA. 5 Important Reaction Flux

Reactions	k[a]	Flux at Indicated Time[b]	
		1.0 (ms)	1.8 (ms)
C3CC. → C2C=C + CH_3	1.07E+04	1.87E-11	7.09E-12
C3CC.+ O_2 → C3CCOO.	4.54E+11	1.14E-09	4.34E-10
C3CCOO. → C3CC.+ O_2	1.19E+04	1.28E-09	4.81E-10
C3CCOO. → C3.CCOOH	1.18E+05	1.27E-08	4.78E-09
C3.CCOOH → C3CCOO.	1.14E+07	5.23E-09	1.96E-09
C3.CCOOH → C2CyCCOC + OH	9.73E+04	4.44E-11	1.67E-11
C3.CCOOH → C2C=C + C.H_2OOH	2.00E+04	9.14E-12	3.43E-12
C3.CCOOH → C=C(C)COOH + CH_3	2.29E+04	1.05E-11	3.93E-12
C3.CCOOH + O_2 → C2C(COOH)COO.	5.68E+11	3.75E-10	1.41E-10
C2C(COOH)COO. → C3.CCOOH + O_2	1.53E+04	3.57E-10	1.33E-10
C2C(COOH)COO. → C2.C(COOH)COOH	4.96E+04	1.16E-09	4.33E-10
C2.C(COOH)COOH → C2C(COOH)COO.	3.41E+07	1.10E-09	4.12E-10
CH_3 + O_2 → CH_3OO.	4.43E+11	1.22E-09	1.46E-09
CH_3OO. → CH_3 + O_2	3.91E+04	4.20E-09	5.14E-09

a k is in unit of s-1 or cm3-mole-1-s-1 and at 700 K and 0.807 atm
b Flux is in unit of mole-sec-cm-3

APPENDIX IB
TRANSITION STATES IN THE NEO-C_5H_{11} + O_2 SYSTEM

TS IB. 1 Thermodynamic Properties from MOPAC PM3 and THERM

SPECIES	H_{f298}[a]	S_{298}[b]	C_p[b]						
			300	400	500	600	800	1000	1500
MOPAC Calculations									
C2CyCCOC	-41.02	77.34	26.78	35.56	43.27	49.57	58.91	65.5	75.54
C3.CCOOH	-20.65	101.74[c]	36.32	45.45	53.22	59.42	68.32	74.46	83.82
C3CCOO.	-16.93	93.62[d]	34.19	42.97	50.69	57.01	66.47	73.23	83.65
TS(1)[e]	1.35	89.83[d]	32.94	42.16	50.06	56.44	65.88	72.62	83.09
TS(2)[f]	15.25	84.06[d]	32.61	42.47	50.9	57.69	67.65	74.59	85.03
THERM Calculations									
C2CyCCOC	-33.33	76.78	26.77	35.71	42.96	49.17	59.1	65.9	0
C3.CCOOH	-12.49	101.28	36.87	45.14	52.29	58.61	67.47	74.22	0
C3CCOO.	-25.39	94.11	35.41	43.62	50.79	57.17	66.25	73.31	0

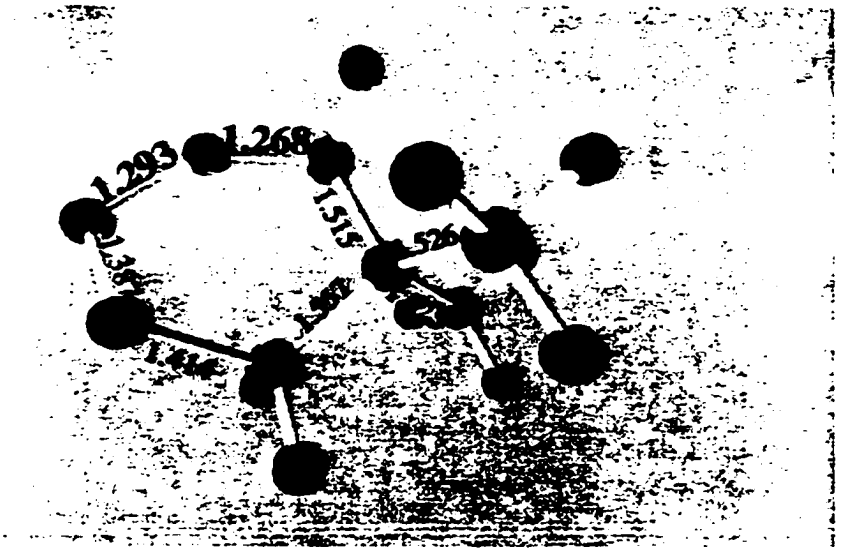
a Unit in kcal-mol^{-1}.
b Unit in cal-mol-1.
c correct for OI & spin degeneracy (Rln2)
d correct for spin degeneracy (Rln2)
e Transition state for reaction C3CCOO. <=> C3.CCOOH
f Transition state for reaction C3.CCOOH <=> C2CyCCOC + OH

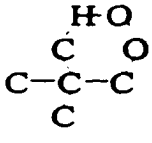
TS IB. 2 Thermodynamic Analysis of Transition State Related Reactions

Rx	C3CCOO. = TS(1)*				
H_{f298} {kcal/mol}	-25.390		-2.690		
S_{298} {cal/mol-K}	93.620		84.060		
ΔH_r {kcal/mol} (298K) = 22.70			ΔH_r avg (298., 1500. K) = 23.23		
ΔS_r {cal/mol K} (298K) = -9.56			ΔS_r avg (298., 1500. K) = -9.13		
A_f/A_r (298 K) = 8.137E-03			A_f/A_r avg (298., 1500. K) = 1.01E-02		
Fit A_f/A_r	A = 2.869E-02	n = -.28	alpha = -7.961E-04		
T (K)	ΔH (kcal/mol)	ΔU (kcal/mol)	ΔS (cal/mol-K)	(A_f/A_r)	ΔG (kcal/mol)
300.00	2.270E+01	2.270E+01	-9.570E+00	8.096E-03	2.557E+01
400.00	2.259E+01	2.259E+01	-9.877E+00	6.937E-03	2.654E+01
500.00	2.258E+01	2.258E+01	-9.908E+00	6.829E-03	2.753E+01
600.00	2.263E+01	2.263E+01	-9.819E+00	7.144E-03	2.852E+01
800.00	2.283E+01	2.283E+01	-9.529E+00	8.267E-03	3.046E+01
1000.00	2.309E+01	2.309E+01	-9.242E+00	9.548E-03	3.233E+01
1200.00	2.335E+01	2.335E+01	-9.002E+00	1.078E-02	3.416E+01
1500.00	2.376E+01	2.376E+01	-8.701E+00	1.254E-02	3.681E+01
2000.00	2.453E+01	2.453E+01	-8.260E+00	1.565E-02	4.105E+01
Rx	**C3.CCOOH = TS(2)***				
H_{f298} {kcal/mol}	-12.490		1.510		
S_{298} {cal/mol-K}	101.740		89.830		
ΔH_r {kcal/mol} (298K) = 14.00			ΔH_r avg (298., 1500. K) = 12.71		
ΔS_r {cal/mol K} (298K) = -11.91			ΔS_r avg (298., 1500. K) = -13.95		
A_f/A_r (298K) = 2.494E-03			A_f/A_r avg (298., 1500. K) = 8.943E-04		
Fit A_f/A_r	A = 4.026E+02	n = -2.17	alpha = -1.197E-03		
T (K)	ΔH (kcal/mol)	ΔU (kcal/mol)	ΔS (cal/mol-K)	(A_f/A_r)	ΔG (kcal/mol)
300.00	1.399E+01	1.399E+01	-1.193E+01	2.467E-03	1.757E+01
400.00	1.365E+01	1.365E+01	-1.291E+01	1.508E-03	1.882E+01
500.00	1.333E+01	1.333E+01	-1.363E+01	1.047E-03	2.015E+01
600.00	1.303E+01	1.303E+01	-1.419E+01	7.925E-04	2.154E+01
800.00	1.249E+01	1.249E+01	-1.496E+01	5.368E-04	2.446E+01
1000.00	1.206E+01	1.206E+01	-1.545E+01	4.206E-04	2.750E+01
1200.00	1.173E+01	1.173E+01	-1.575E+01	3.613E-04	3.063E+01
1500.00	1.141E+01	1.141E+01	-1.599E+01	3.207E-04	3.539E+01
2000.00	1.132E+01	1.132E+01	-1.605E+01	3.112E-04	4.341E+01

* TS(1) & TS(2) are the same as in Table 2a and Table 2b

TS IB. 3 Transition State (TS1) Structure and its Properties



Properties Of Transition State (TS1)							
TS(1)		Principal Moments of Inertial (cm^{-1}) A = 0.1336 B = 0.0643 C = 0.0614 Principal Moments of Initial (10^{-40} g-cm^2) A = 209.510 B = 435.256 C = 455.821 Symmetry = 9 Barrier for Rotors CH3--(CC3OOH) = 4.7 kJ/mole					
Frequencies (cm^{-1})							
-2767	81	178	203	264	309	330	418
448	464	496	548	672	690	875	946
959	965	977	988	1009	1057	1096	1126
1148	1235	1280	1320	1331	1360	1378	1400
1401	1402	1406	1413	1415	1417	2959	3038
3080	3080	3084	3085	3111	3134	3177	3178

TS IB. 4 Transition State's Z-Matrix (TS1) for MOPAC Calculation

PM3 PRECISE TS THERMO(298,1498,100) ROT=9 TRANS=3
Input Z-Matrix for MOPAC Calculation
Transition States for Reaction C3CCOO. → C3.CCOOH

ATOM NUMBER (I)	CHEMICAL SYMBOL	BOND LENGTH (ANGSTROMS) NA:I	BOND ANGLE (DEGREES) NB:NA:I	TWIST ANGLE (DEGREES) NC:NB:NA:I	NA	NB	NC
1	C						
2	C	1.52517 *		1			
3	C	1.52638 *	109.34890 *	2	1		
4	C	1.55659 *	108.60235 *	-119.74564 *	2	1	3
5	C	1.51519 *	110.36392 *	121.35379 *	2	1	3
6	H	1.26814 *	107.69587 *	138.24071 *	5	2	1
7	O	1.29247 *	144.06736 *	-22.25409 *	6	5	2
8	O	1.41415 *	111.58871 *	-164.70251 *	4	2	1
9	H	1.09854 *	111.78460 *	-179.48823 *	1	2	3
10	H	1.09798 *	111.18068 *	60.28528 *	1	2	3
11	H	1.09783 *	111.09187 *	-59.41340 *	1	2	3
12	H	1.09821 *	111.25955 *	60.63817 *	3	2	1
13	H	1.09827 *	111.36133 *	-59.15849 *	3	2	1
14	H	1.09780 *	111.38918 *	-179.30266 *	3	2	1
15	H	1.10306 *	112.40537 *	81.98248 *	4	2	1
16	H	1.10663 *	110.69537 *	-39.79590 *	4	2	1
17	H	1.09202 *	115.26263 *	23.95895 *	5	2	1
18	H	1.09182 *	115.66422 *	-107.95967 *	5	2	1

TS IB. 5 Interatomic Distances (TS1) from MOPAC Calculation

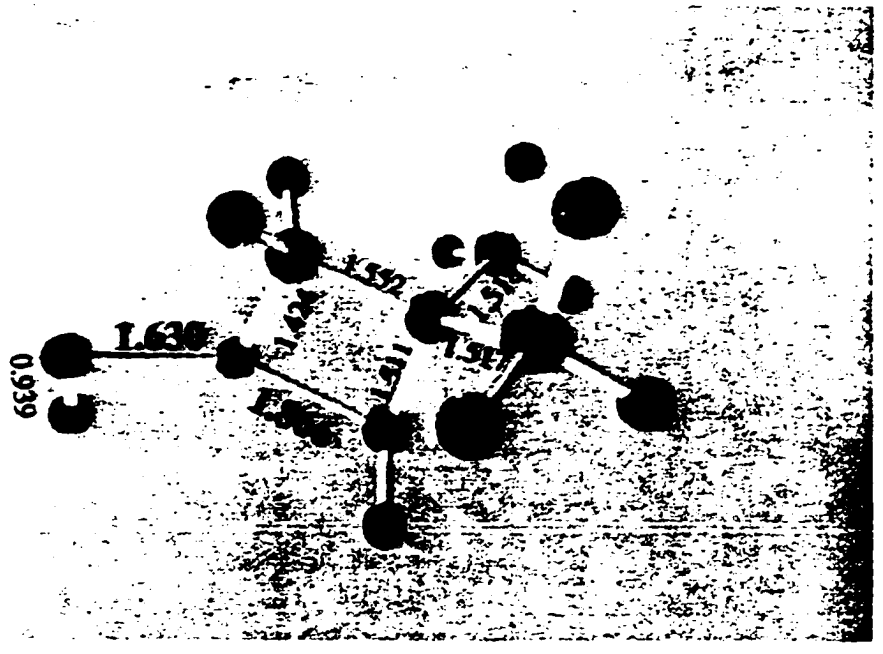
		C1	C2	C 3	C4	C 5	H 6
C	1	.000000					
C	2	1.525169	.000000				
C	3	2.489701	1.526384	.000000			
C	4	2.502746	1.556586	2.521677	.000000		
C	5	2.496047	1.515188	2.494243	2.494134	.000000	
H	6	3.463071	2.252127	3.171443	2.452441	1.268136	.000000
O	7	4.113112	2.886904	3.796703	2.297329	2.435755	1.292468
O	8	3.749201	2.458179	3.096599	1.414151	2.767027	2.086142
H	9	1.098543	2.185526	3.464022	2.765698	2.753286	3.563122
H	10	1.097983	2.177570	2.748419	2.745619	3.460014	4.308334
H	11	1.097830	2.176342	2.739946	3.476815	2.772790	3.953867
H	12	2.752895	2.179799	1.098206	3.492593	2.764087	3.686681
H	13	2.742481	2.181121	1.098272	2.775461	3.460634	4.079607
H	14	3.460109	2.181115	1.097805	2.778882	2.753146	3.052027
H	15	2.964337	2.224546	2.644636	1.103061	3.445008	3.453726
H	16	2.605179	2.205694	3.462164	1.106627	2.921558	2.852976
H	17	2.597860	2.213725	3.410232	3.088626	1.092020	1.850047
H	18	3.197650	2.218292	2.568179	3.361477	1.091820	1.842622

		O7	O8	H9	H 10	H 11	H 12
O	7	.000000					
O	8	1.387168	.000000				
H	9	4.113133	3.981394	.000000			
H	10	4.762313	4.115381	1.772121	.000000		
H	11	4.836175	4.599323	1.771191	1.770999	.000000	
H	12	4.556924	4.070258	3.766989	3.114295	2.545435	.000000
H	13	4.497554	3.531583	3.763930	2.543197	3.085103	1.770324
H	14	3.534835	2.824883	4.329862	3.759807	3.758861	1.772126
H	15	3.182593	1.959723	3.395241	2.796200	3.935739	3.701705
H	16	2.576883	2.091746	2.420250	2.842782	3.662412	4.328535
H	17	2.922361	3.501154	2.457203	3.668958	2.769106	3.550266
H	18	3.087107	3.433577	3.633149	4.131434	3.165453	2.502324

TS IB. 5 Interatomic Distances (TS1) from MOPAC Calculation (Cont')

		H13	H14	H15	H16H17	H18	
H	13	.000000					
H	14	1.772320	.000000				
H	15	2.461169	2.878459	.000000			
H	16	3.670986	3.846308	1.795679	.000000		
H	17	4.296174	3.815352	4.112881	3.143349	.000000	
H	18	3.653773	2.634277	4.183693	3.951492	1.800672	.000000

TS IB. 6 Transition State Structure (TS2) and its Properties



Properties Of Transition State (TS2)		
TS(2)	OH C--O C–C–C C	Principal Moments of Initial (cm^{-1}) A = 0.1568 B = 0.0529 C = 0.0512 Principal Moments of Initial (10^{-40} g-cm^2) A = 178.544 B = 529.411 C = 546.385 Symmetry = 9 Barrier for Rotors: CH3--(CC3OOH) = 4.7 kJ/mole OH--(C2CyCCOC) = 0.0 kJ/mole

Frequencies (cm^{-1})							
-998	63	145	157	158	183	270	326
345	449	454	515	653	714	915	932
937	945	964	971	991	1004	1027	1074
1173	1241	1288	1321	1321	1370	1393	1400
1402	1403	1412	1415	1427	2968	3017	3081
3083	3083	3084	3122	3143	3177	3178	4001

TS IB. 7 Transition State (TS2) Z-Matrix for MOPAC Calculation

PM3 T=36000 PRECISE TS THERMO(298,1498,100) ROT=6 TRANS=4
TSC2YC3O.DAT=TC2YC3OB.ARC+thermo see if get the same result as PC

ATOM NUMBER (I)	CHEMICAL SYMBOL	BOND LENGTH (ANGSTROMS) NA:I	BOND ANGLE (DEGREES) NB:NA:I	TWIST ANGLE (DEGREES) NC:NB:NA:I	NA	NB	NC
1	C						
2	C	1.51803 *		1			
3	C	1.51794 *	110.43310 *	2	1		
4	C	1.55149 *	112.42165 *	-126.49523 *	2	1	3
5	C	1.51128 *	112.69436 *	127.05850 *	2	1	3
6	O	1.86516 *	81.76388 *	114.76459 *	5	2	1
7	O	1.63063 *	151.14749 *	122.80247 *	6	5	2
8	H	1.09816 *	111.69155 *	-179.67800 *	1	2	3
9	H	1.09784 *	111.02266 *	60.25231 *	1	2	3
10	H	1.09778 *	111.11311 *	-59.53770 *	1	2	3
11	H	1.09778 *	111.11429 *	59.32907 *	3	2	1
12	H	1.09780 *	111.02746 *	-60.48985 *	3	2	1
13	H	1.09824 *	111.64831 *	179.43962 *	3	2	1
14	H	1.10412 *	113.93878 *	127.49080 *	4	2	1
15	H	1.10309 *	114.64780 *	1.81371 *	4	2	1
16	H	1.08920 *	119.72112 *	12.13858 *	5	2	1
17	H	1.08854 *	119.41148 *	-138.80923 *	5	2	1
18	H	0.93888 *	91.99001 *	70.99032 *	7	6	5

TS IB. 8 Interatomic Distance of TS2 from MOPAC Calculation

		C 1	C 2	C 3	C 4	C 5	O 6
C	1	.000000					
C	2	1.518041	.000000				
C	3	2.549899	1.551652	.000000			
C	4	2.493865	1.517850	2.552322	.000000		
C	5	2.522112	1.511203	2.265579	2.521621	.000000	
O	6	3.297928	2.226444	1.424285	3.356076	1.865534	.000000
H	7	1.097762	2.170367	3.507204	2.746716	2.857376	4.094420
H	8	1.097869	2.169141	2.855994	2.759682	3.471522	3.933033
H	9	1.098164	2.177824	2.777116	3.462720	2.743016	3.242497
H	10	2.619543	2.247583	1.103113	3.353695	3.062035	2.082843
H	11	3.369477	2.239857	1.104108	2.610736	3.027075	2.109135
H	12	2.756034	2.169899	3.507861	1.097773	2.846695	4.134907
H	13	3.462514	2.177138	2.771680	1.098236	2.750004	3.341459
H	14	2.750474	2.169222	2.868225	1.097803	3.472352	3.992638
H	15	3.433370	2.254514	2.967182	2.682426	1.088550	2.437927
H	16	2.687493	2.258884	2.977427	3.431399	1.089183	2.391726
O	17	4.814153	3.687595	2.469663	4.536300	3.386186	1.630273
H	18	5.188222	4.110177	3.105625	5.055716	3.467762	1.909510

		H 7	H 8	H 9	H 10	H 11	H 12
H	7	.000000					
H	8	1.772402	.000000				
H	9	1.771870	1.771857	.000000			
H	10	3.703394	2.680394	2.560526	.000000		
H	11	4.273396	3.455621	3.778347	1.789889	.000000	
H	12	2.552332	3.125320	3.766009	4.267523	3.691170	.000000
H	13	3.764063	3.770644	4.324130	3.752412	2.516166	1.771883
H	14	3.096044	2.560443	3.768856	3.428796	2.711632	1.772698
H	15	3.595268	4.332995	3.792852	3.926168	3.441690	2.854660
H	16	2.869779	3.753330	2.544106	3.504394	3.907682	3.580120
O	17	5.678565	5.279233	4.734729	2.907811	2.531641	5.431803
H	18	5.968555	5.793310	4.993579	3.538239	3.355151	5.841028

TS IB. 8 Interatomic Distance of TS2 from MOPAC Calculation

		H 13	H 14	H 15	H 16	O 17	H 18
H	13	.000000					
H	14	1.772143	.000000				
H	15	2.547123	3.749952	.000000			
H	16	3.798785	4.331582	1.833478	.000000		
O	17	4.225636	5.033353	3.645269	3.912016	.000000	
H	18	4.748895	5.683758	3.652430	3.798991	.938890	.000000

APPENDIX IC

FIGURES IN THE NEO-C_5H_{11} + O_2 SYSTEM

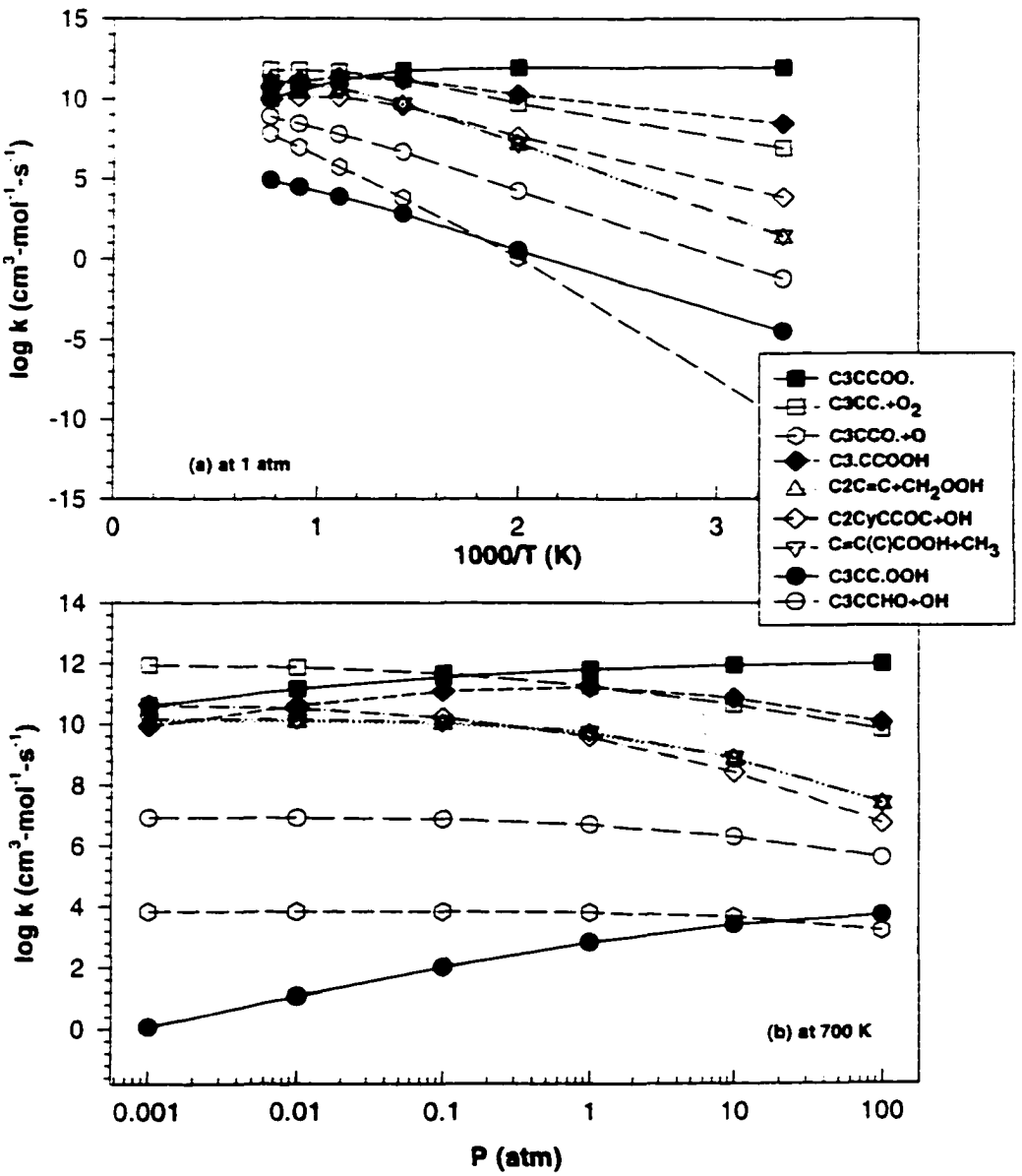


Figure IC. 1 Temperature and pressure dependence of rate constants of the various channels of C3CC. + O_2 with He as bath gas

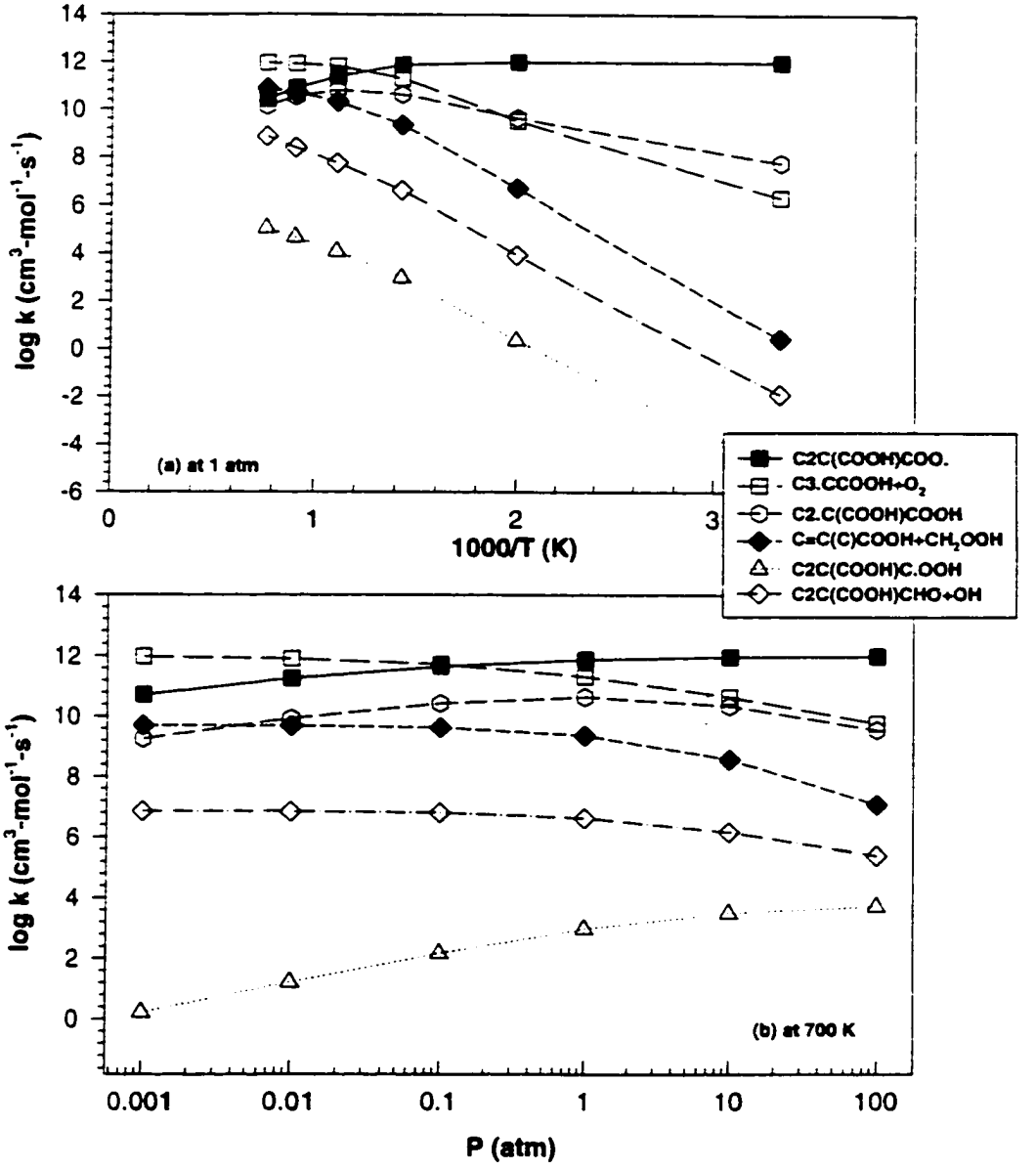


Figure IC. 2 Temperature and pressure dependence of rate constants of the various channels of C3.CCOOH + O_2 with He as bath gas

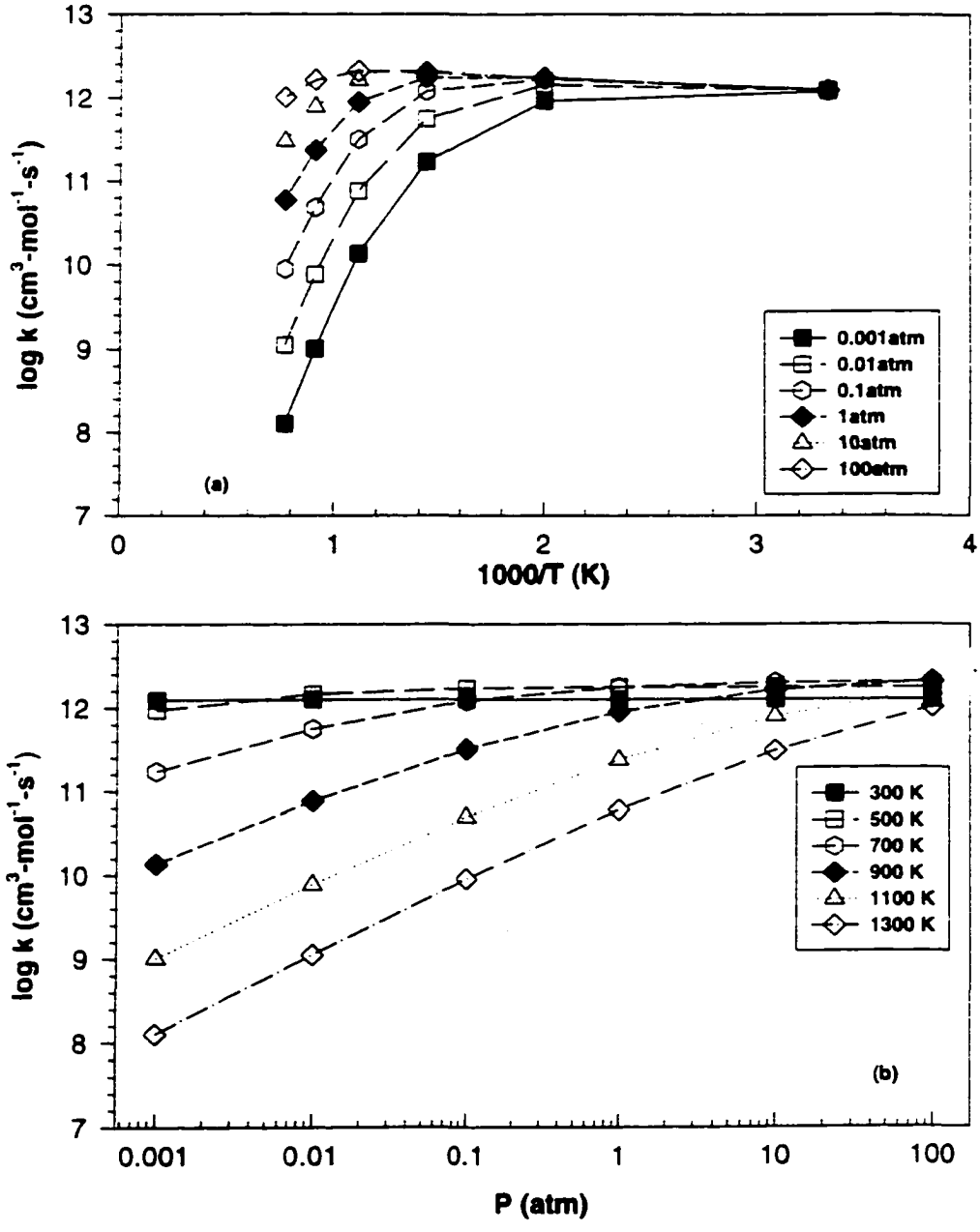


Figure IC. 3 Temperature and pressure dependence of reaction C2C=C + OH → C3.COH with He as bath gas

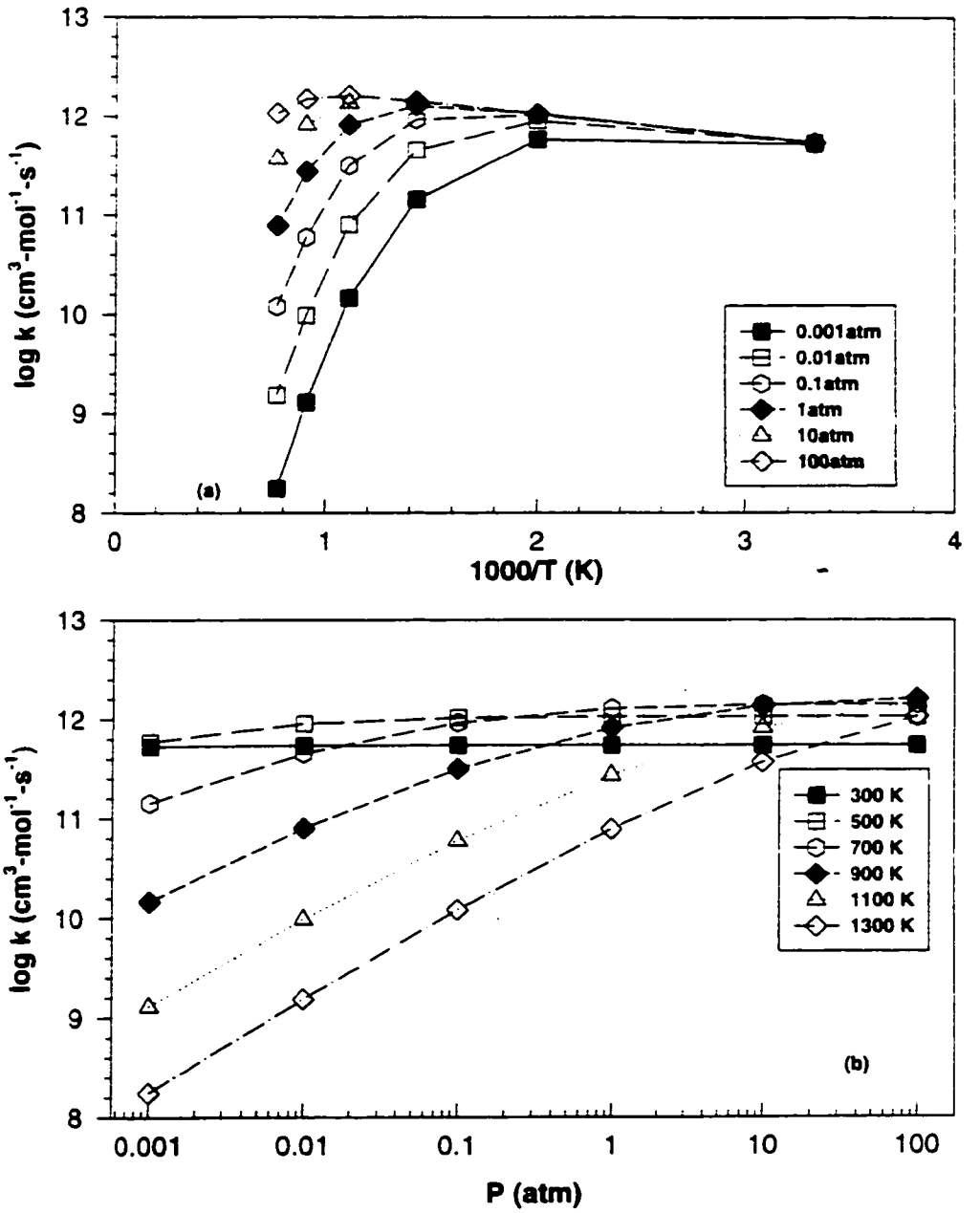


Figure IC. 4 Temperature and pressure dependence of reaction C2C=C + OH → C3.COH with He as bath gas

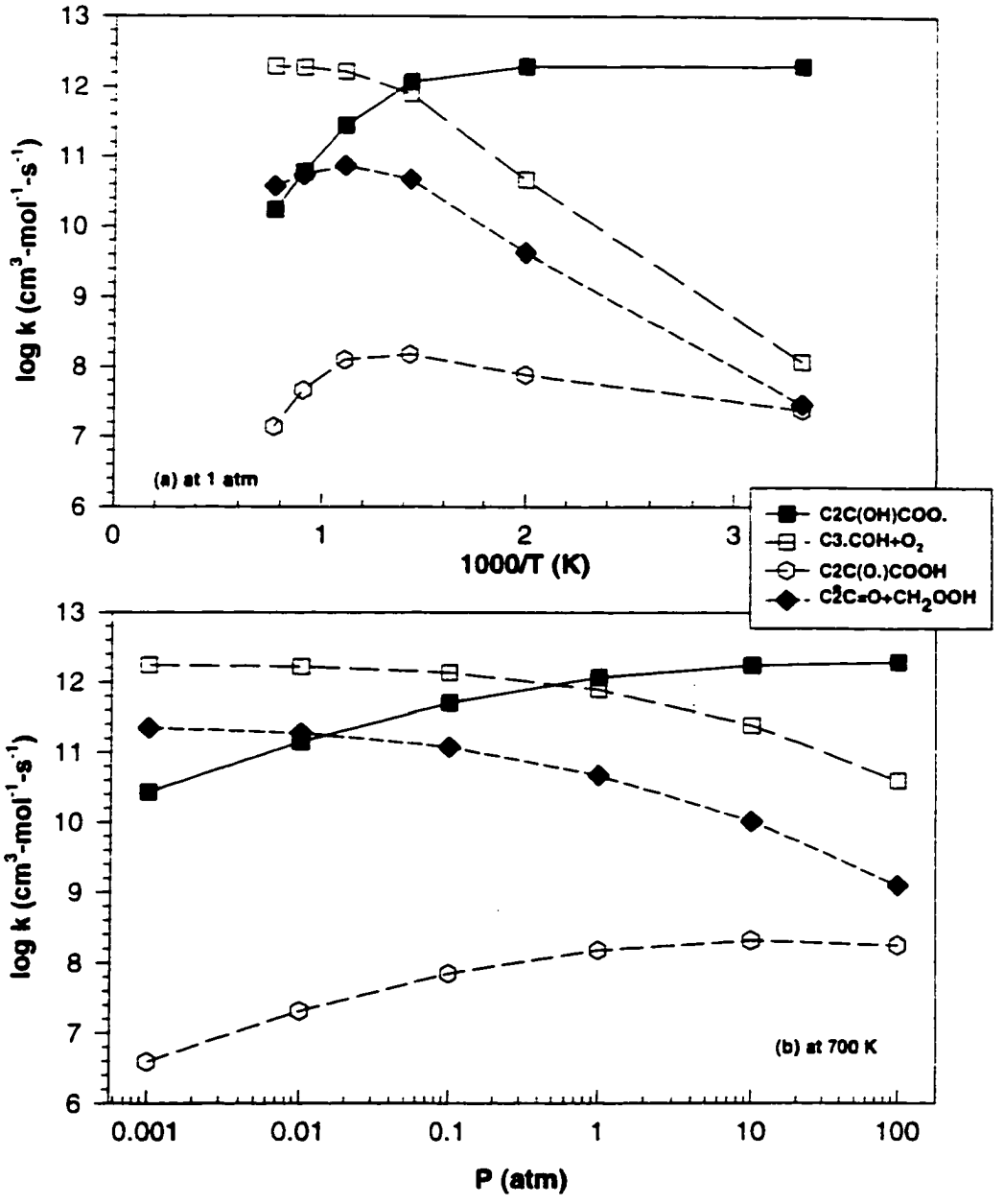


Figure IC. 5 Temperature and pressure dependence of rate constants of the various channels of C3.COH + O_2 with He as bath gas

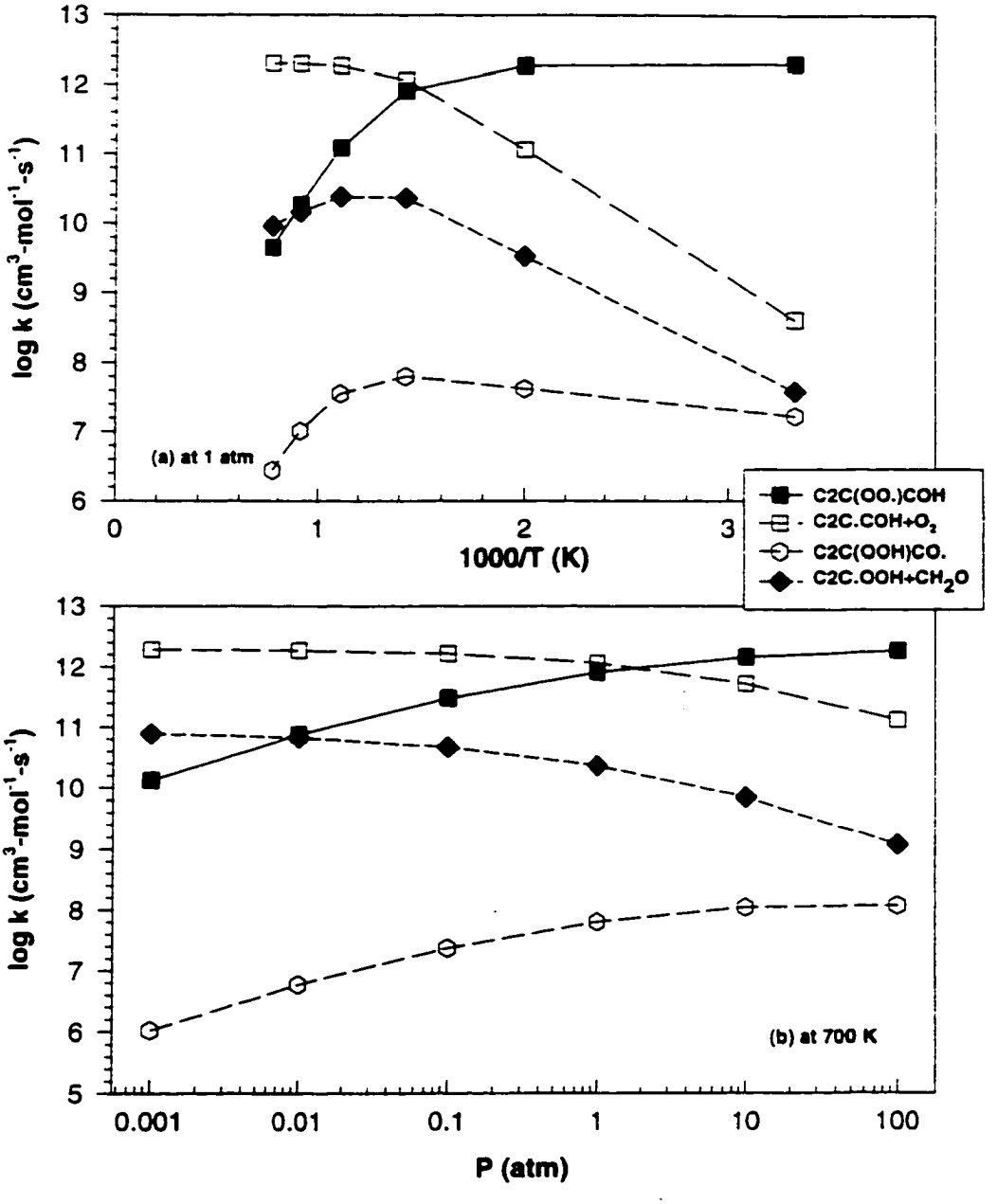


Figure IC. 6 Temperature and pressure dependence of rate constants of the various channels of C2C.COH + O_2 with He as bath gas

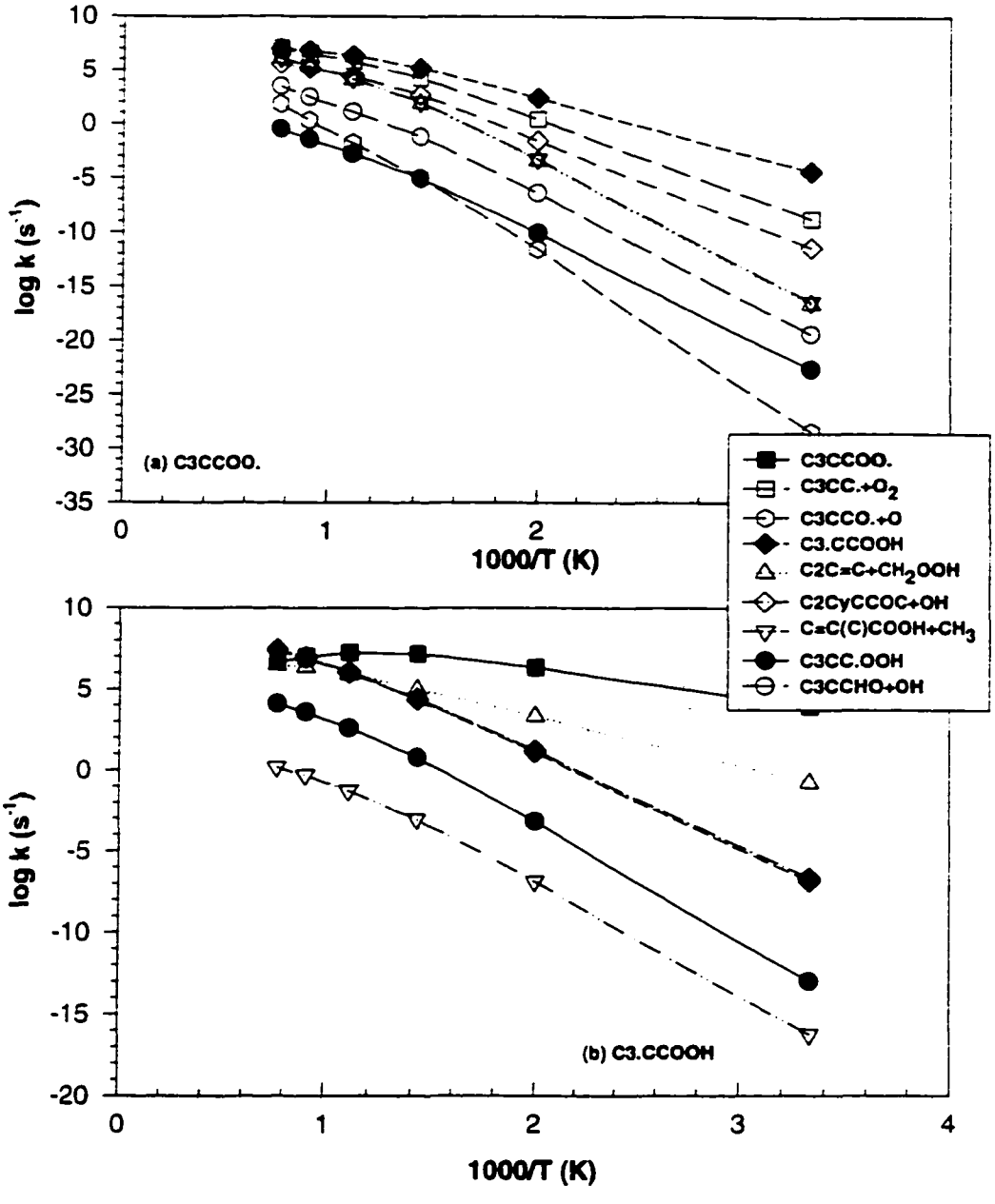


Figure IC. 7 Temperature dependence of rate constants of the various channels of stabilized adducts C3CCOO. / C3.CCOOH with He as bath gas

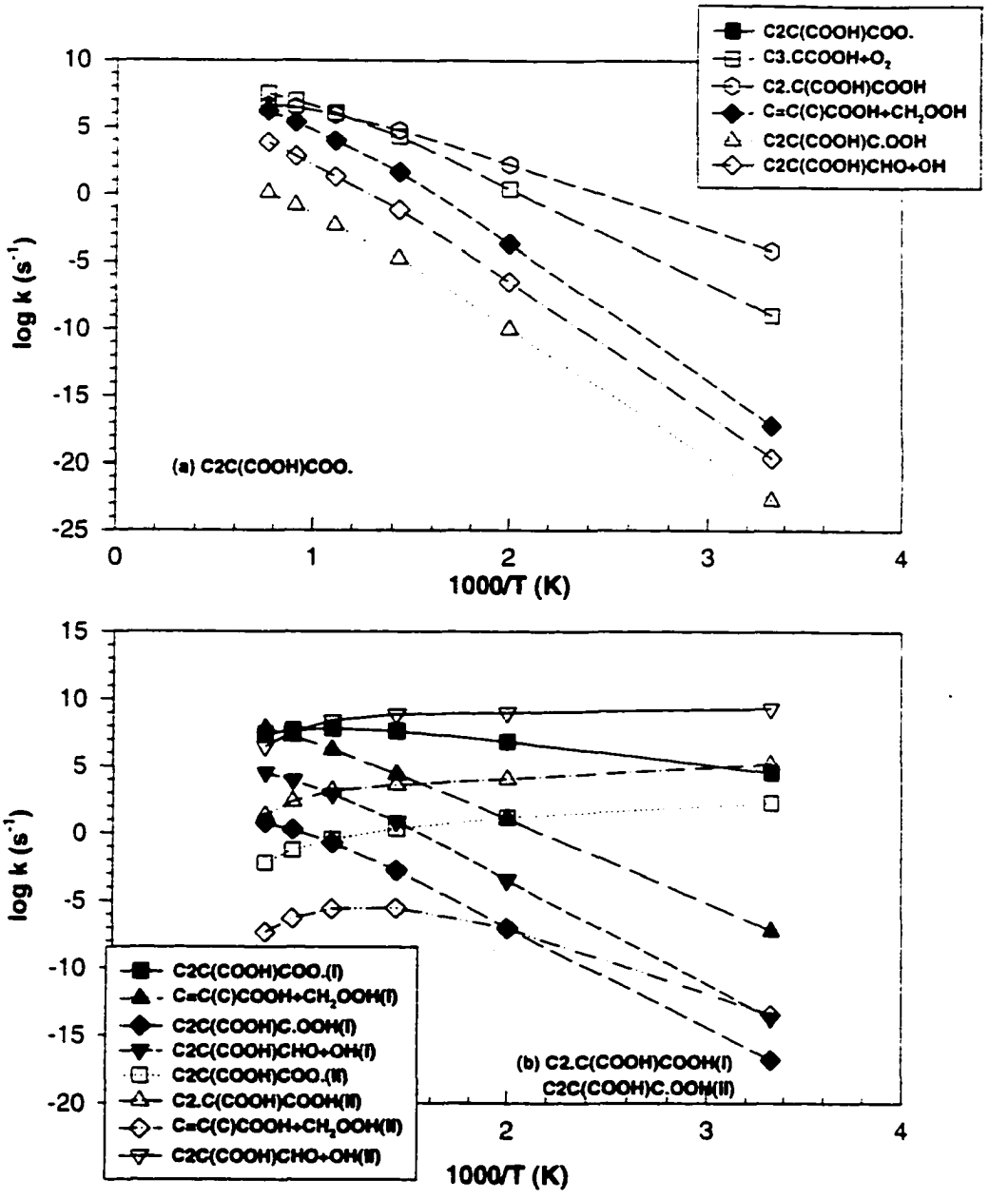


Figure IC. 8 Temperature dependence of rate constants of the various channels of stabilized adducts C2C(COOH)COO. / C2.C(COOH)COOH / C2C(COOH)C.OOH with He as bath gas

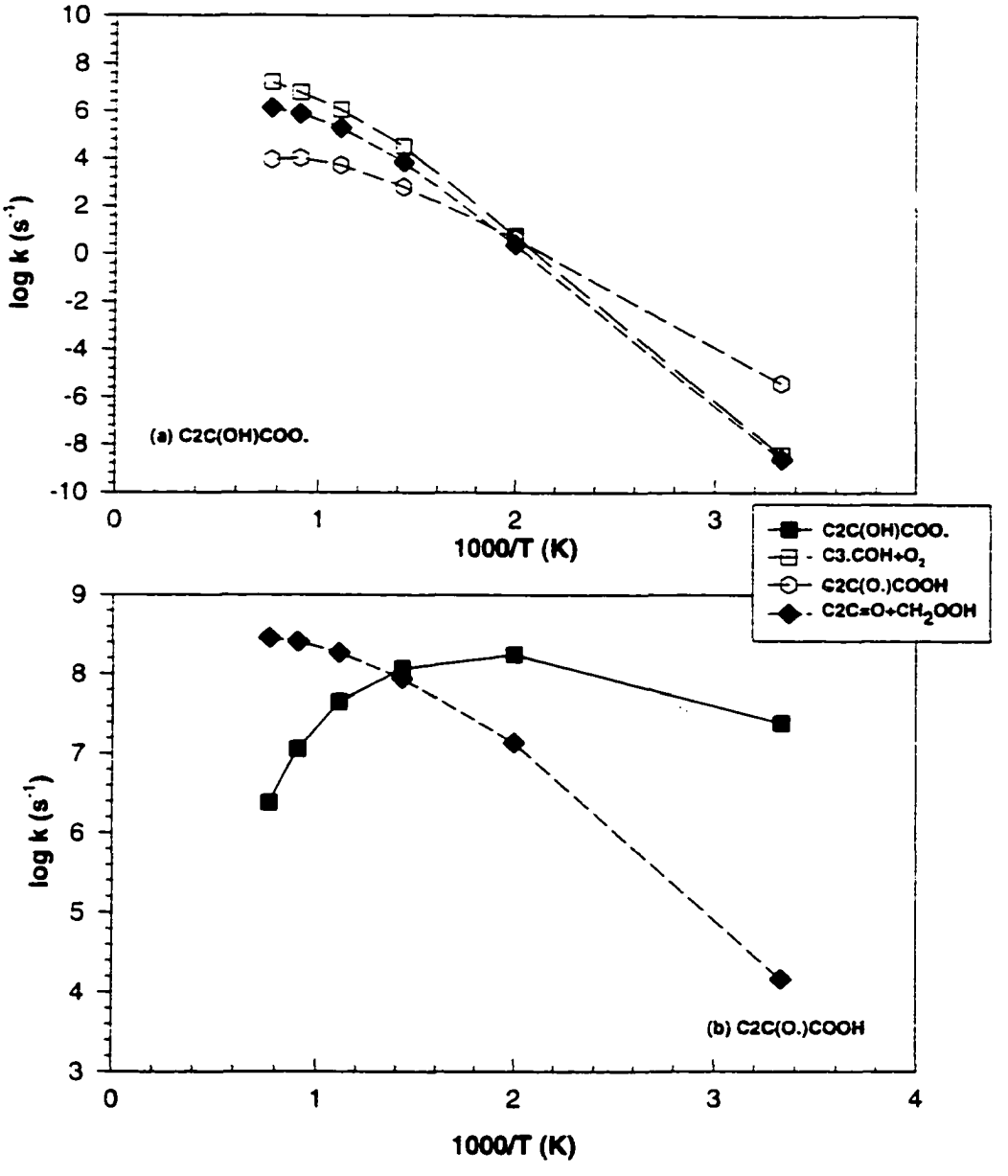


Figure IC. 9 Temperature dependence of rate constants of the various channels of stabilized adducts C2C(OH)COO. / C2C(O.)COOH with He as bath gas

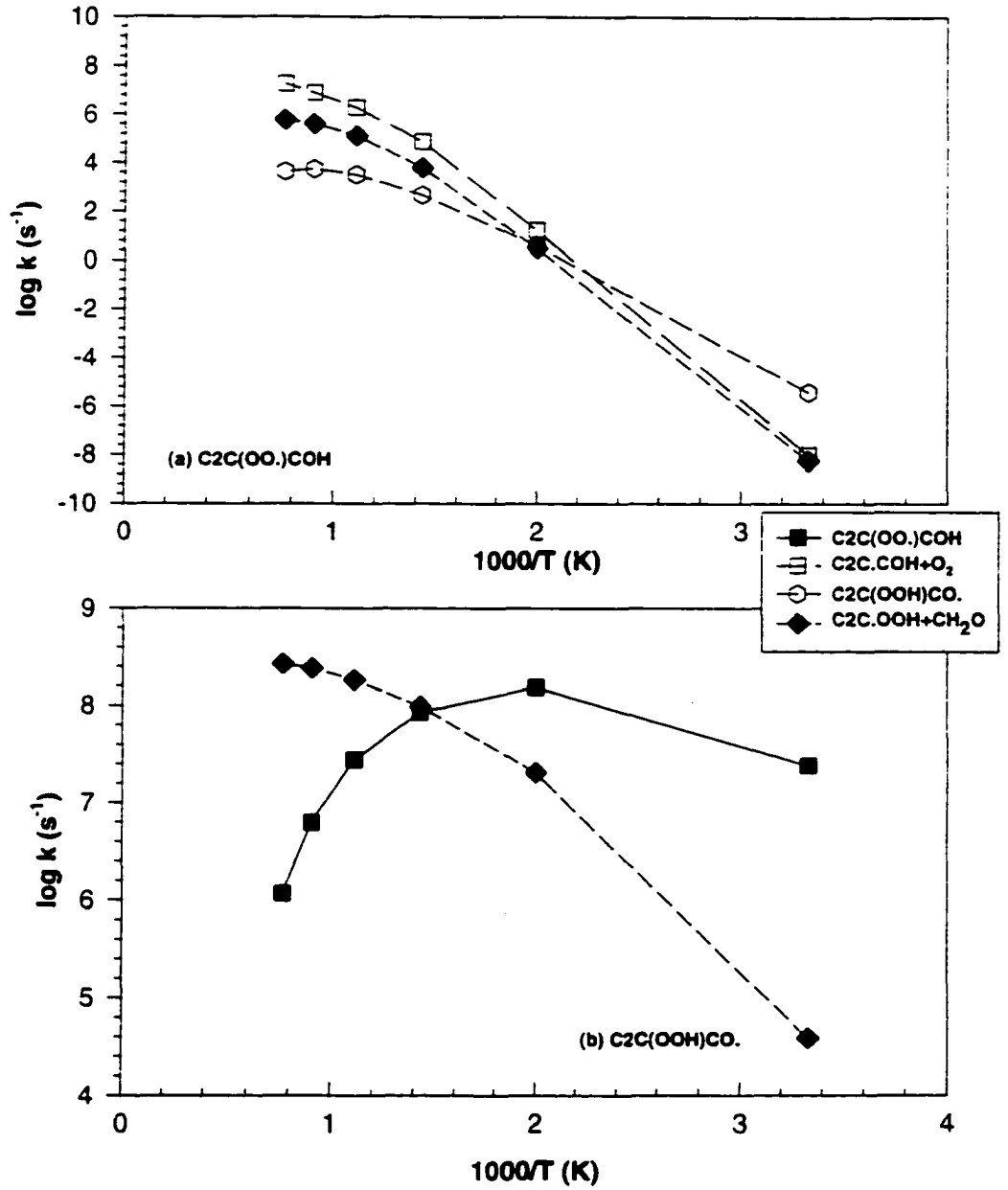


Figure IC. 10 Temperature dependence of rate constants of the various channels of stabilized adducts C2C(OO.)COH / C2C(OOH)CO. with He as bath gas

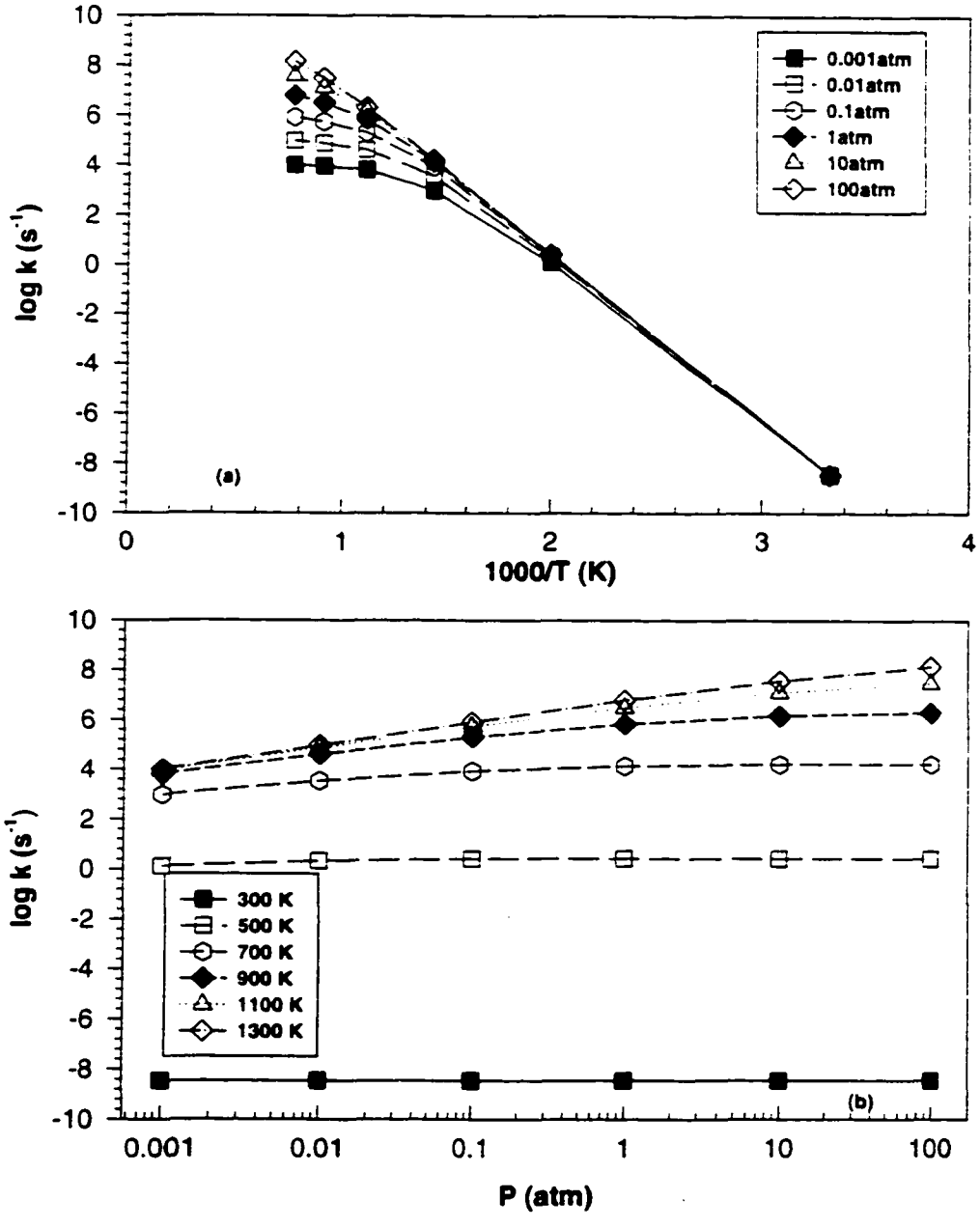


Figure IC. 11 Temperature and pressure dependence of reaction C3CC. → C2C=C + CH_3 with He as bath gas

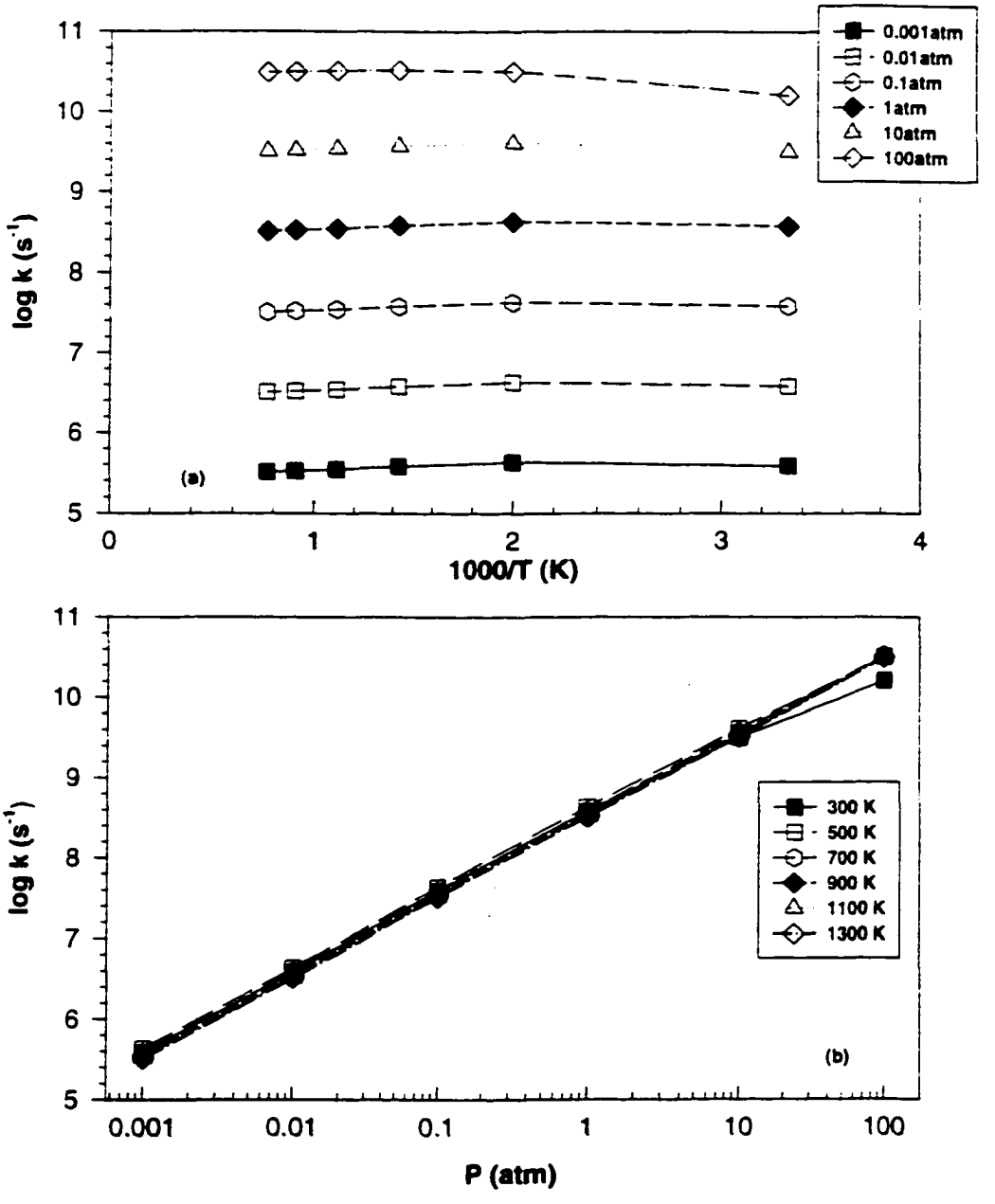


Figure IC. 12 Temperature and pressure dependence of reaction $CH_2OOH \rightarrow CH_2O + OH$ with He as bath gas

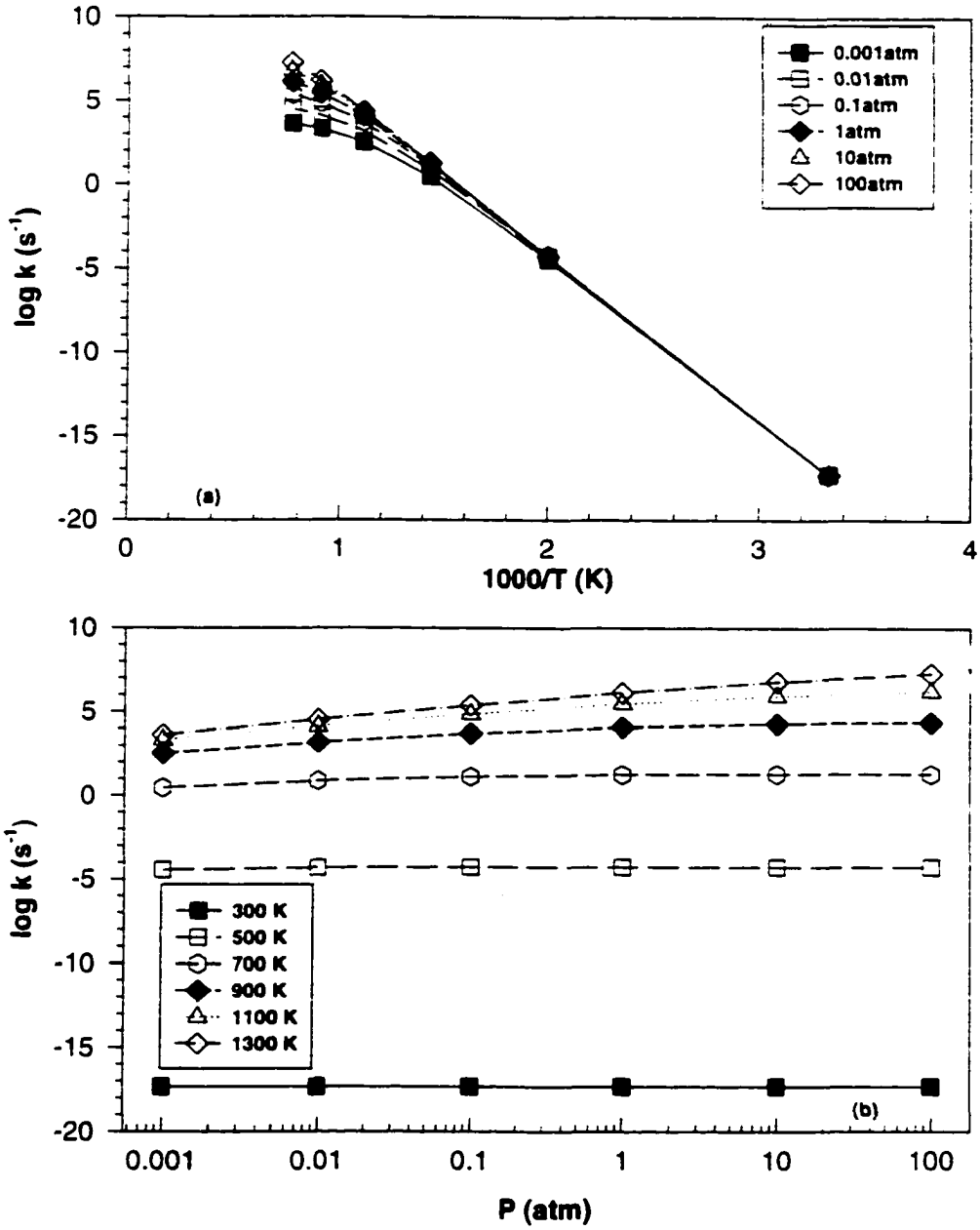


Figure IC. 13 Temperature and pressure dependence of reaction C=C(C)COOH → C=C(C)CO. + OH with He as bath gas

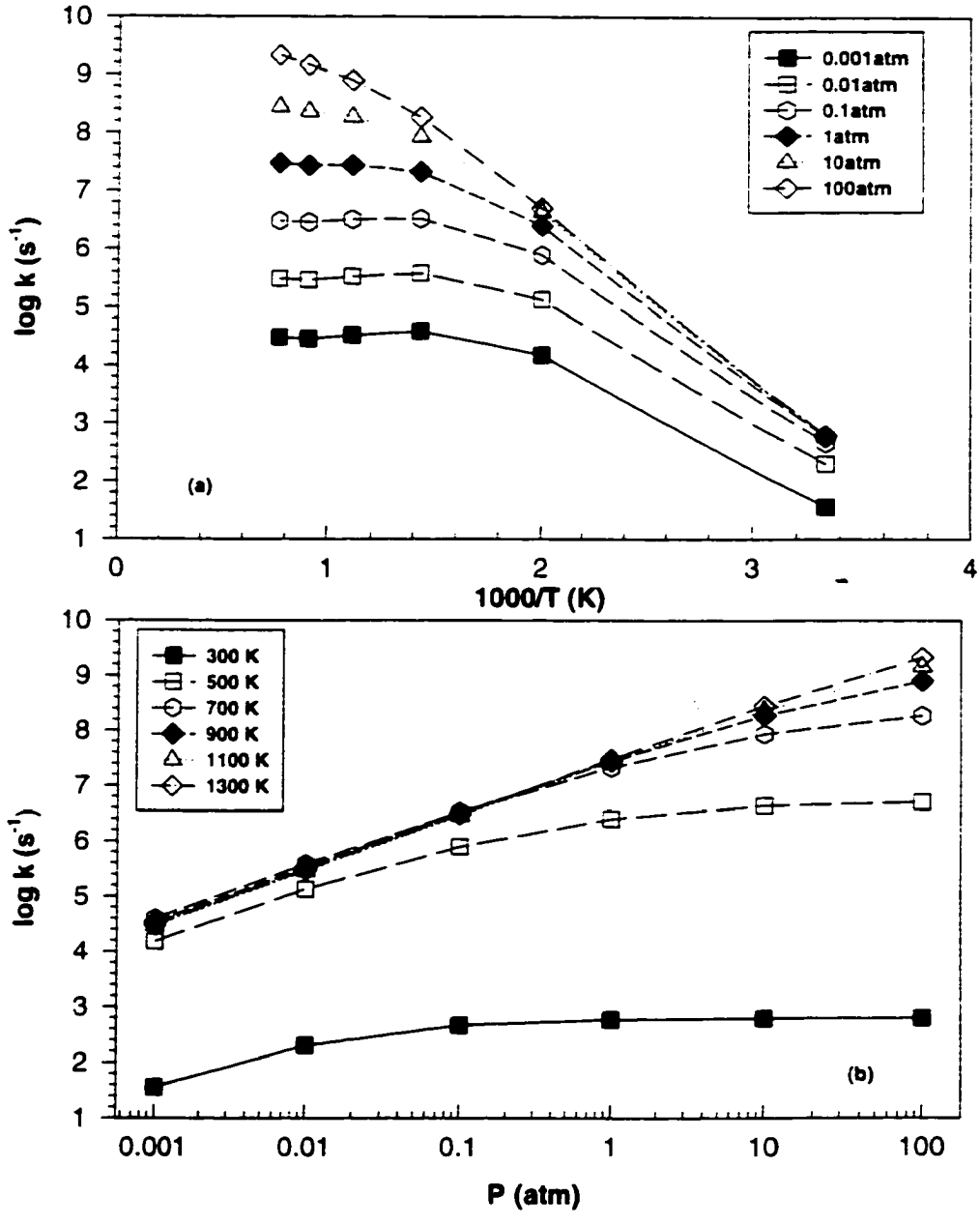


Figure IC. 14 Temperature and pressure dependence of reaction C=C(C)CO. → C=C(C)CHO + H with He as bath gas

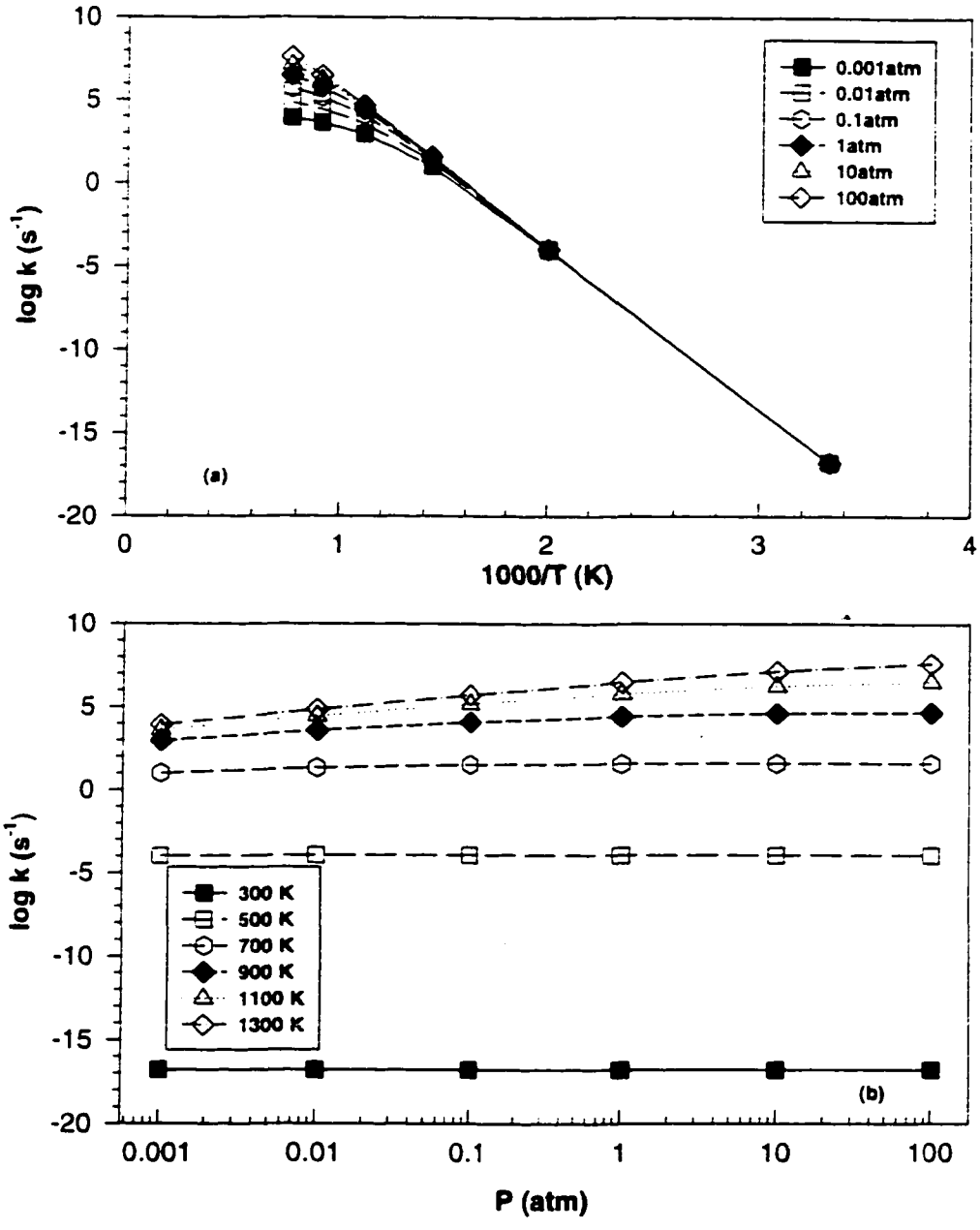


Figure IC. 15 Temperature and pressure dependence of reaction C2C(COOH)CHO → C2C(CO.)CHO + OH with He as bath gas

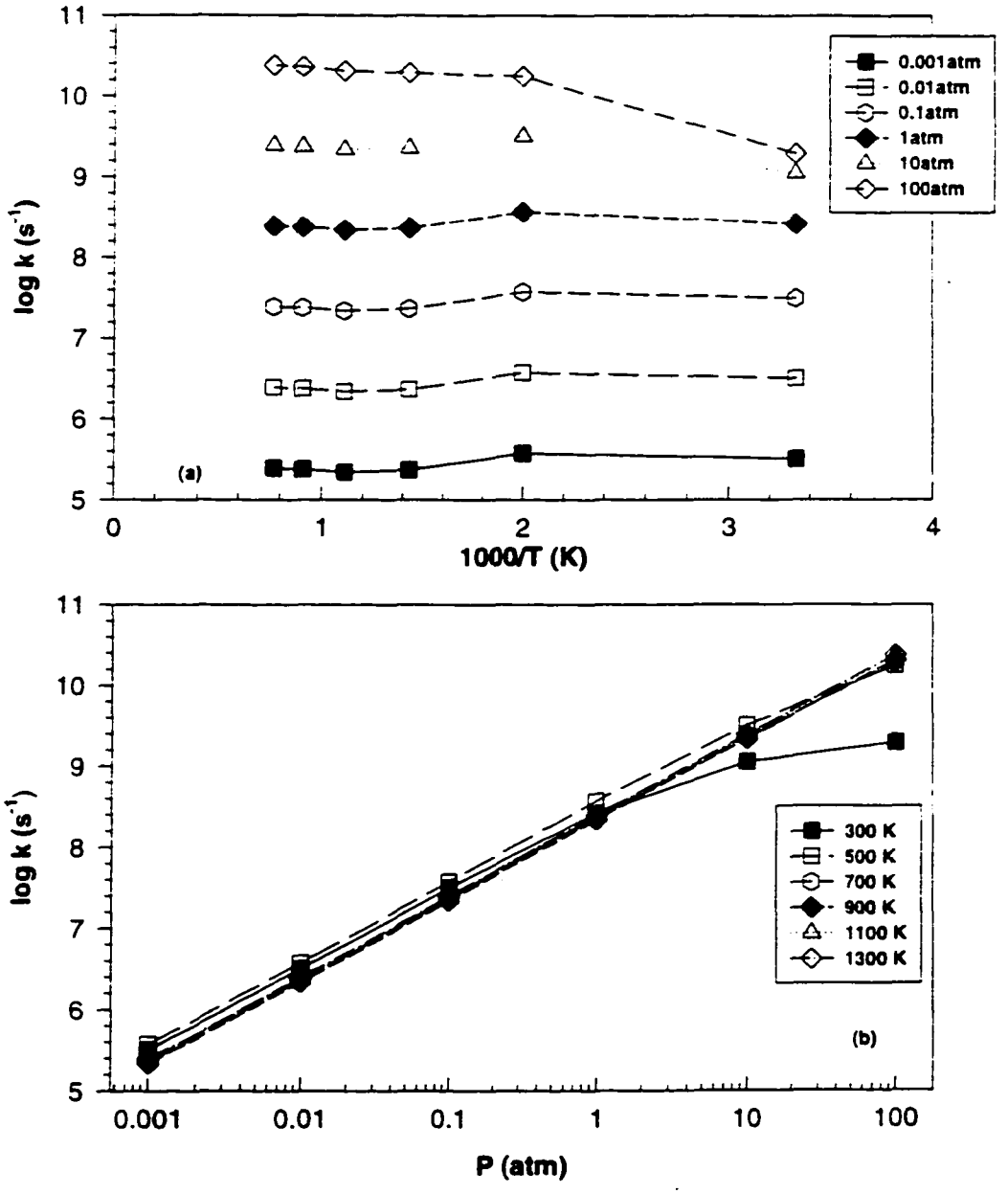


Figure IC. 16 Temperature and pressure dependence of reaction C2C(CO.)CHO → C2C.CHO + CH_2O with He as bath gas

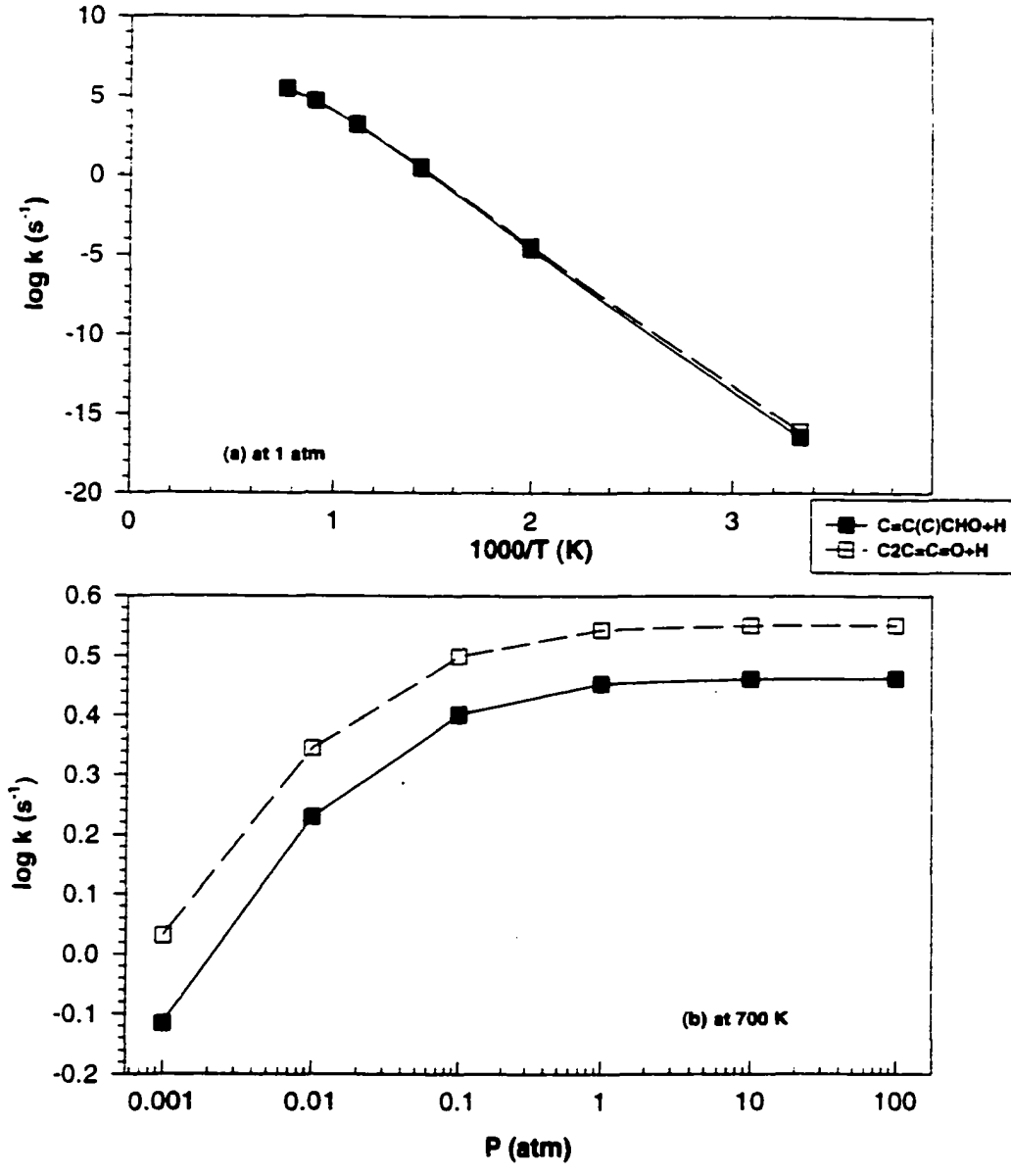


Figure IC. 17 Temperature and pressure dependence of reaction C2C.CHO → Products with He as bath gas

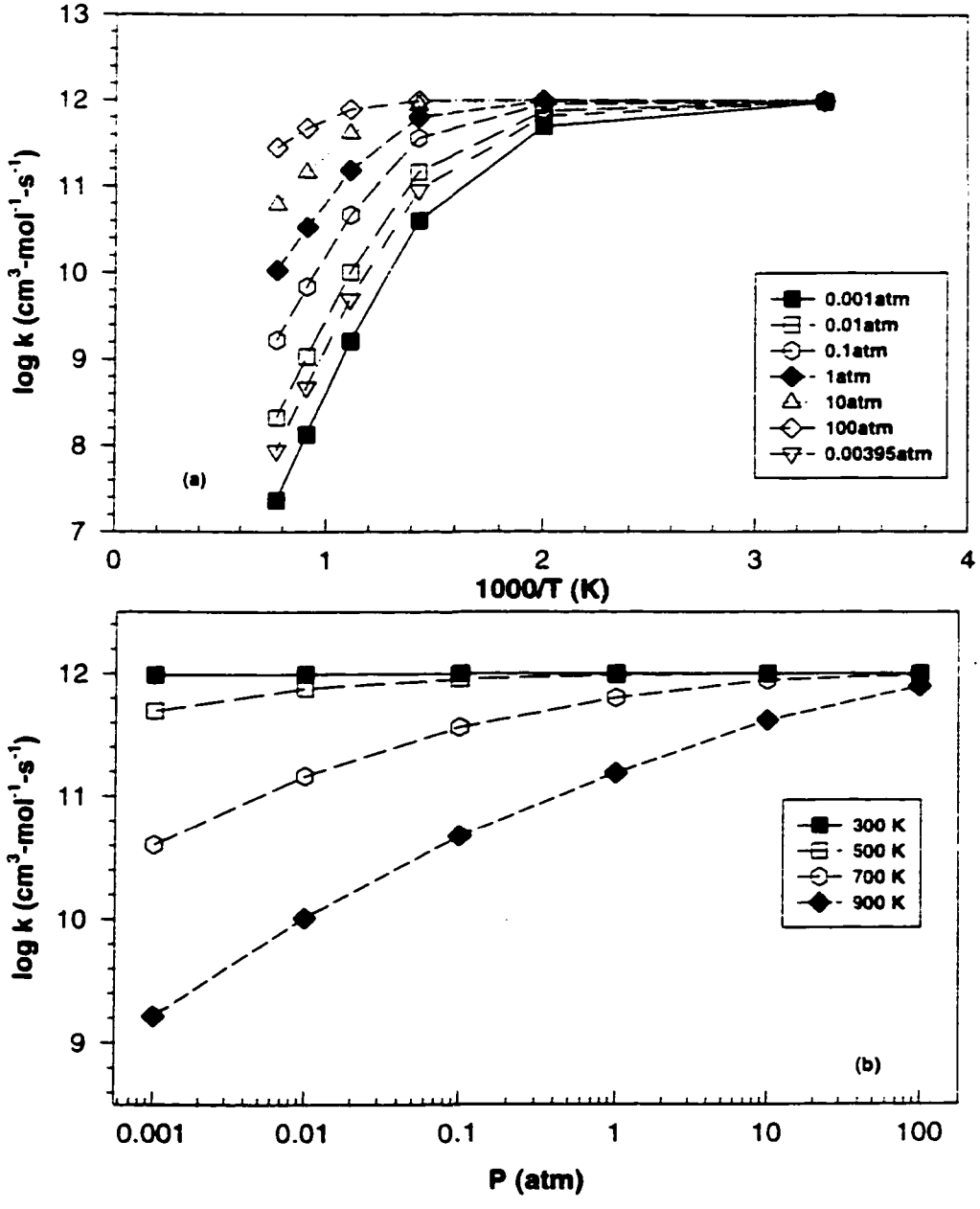


Figure IC. 18 Fall-off in the reaction C3CC. + O_2 → C3CCOO.

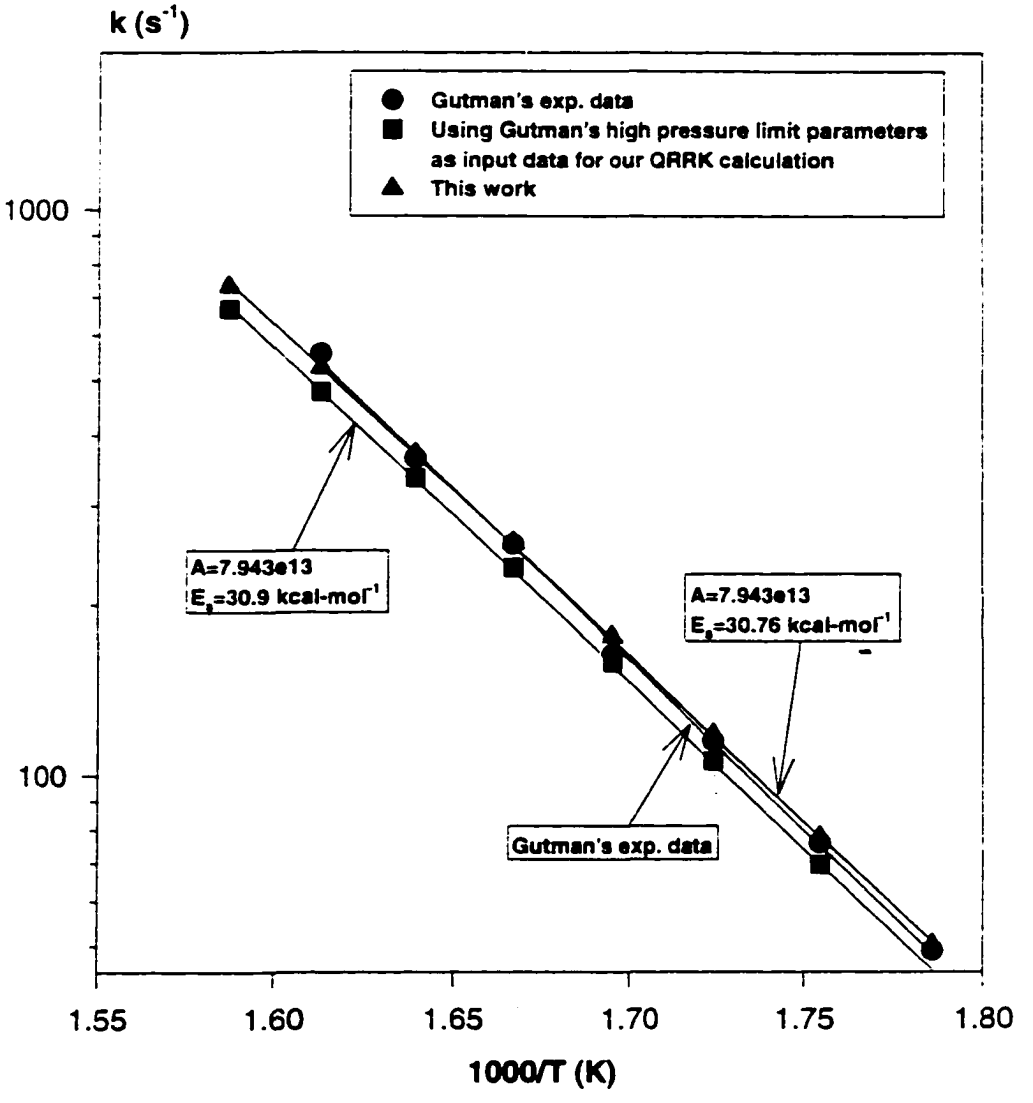


Figure IC. 19 Comparison with Gutman's experimental result

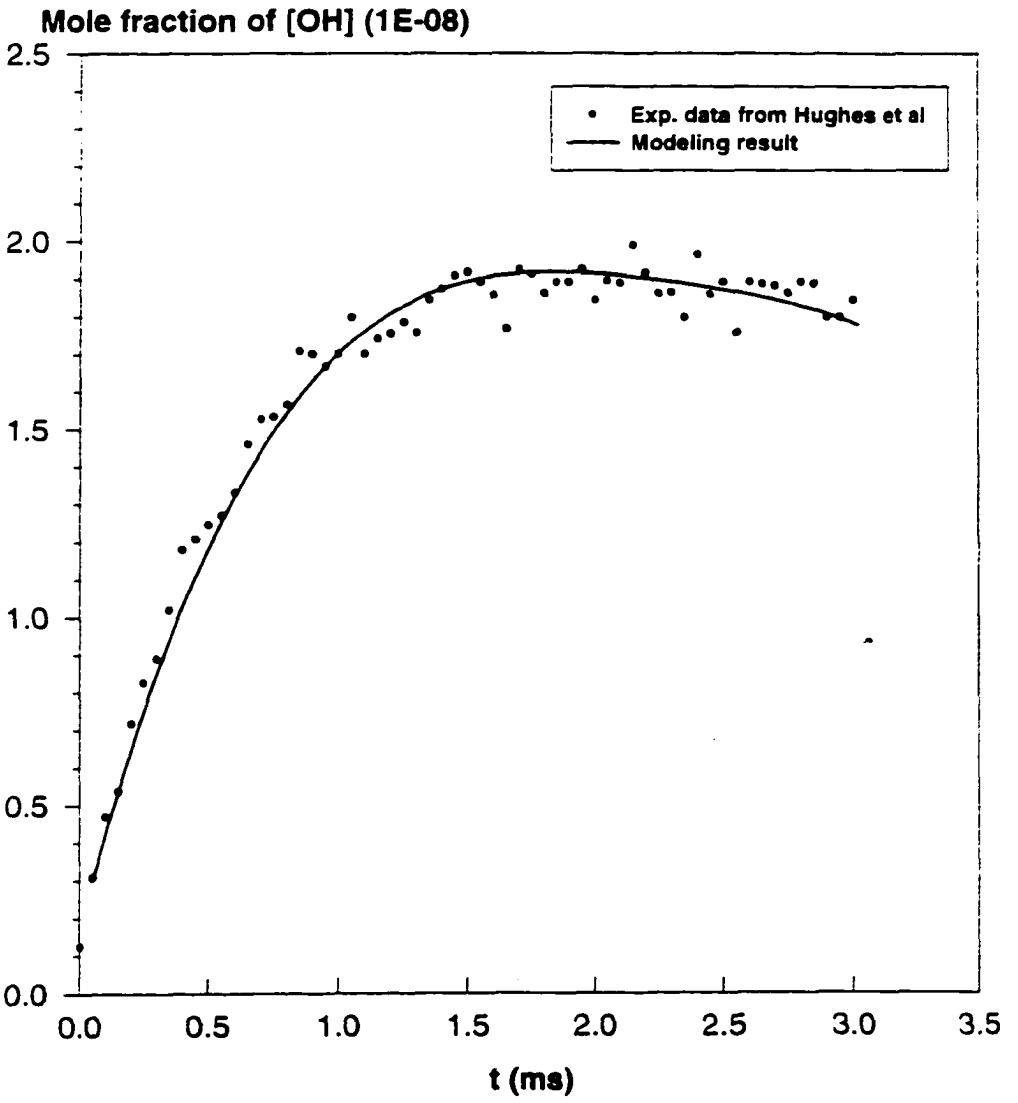


Figure IC. 20 OH formation comparison of model with Hughes experiment

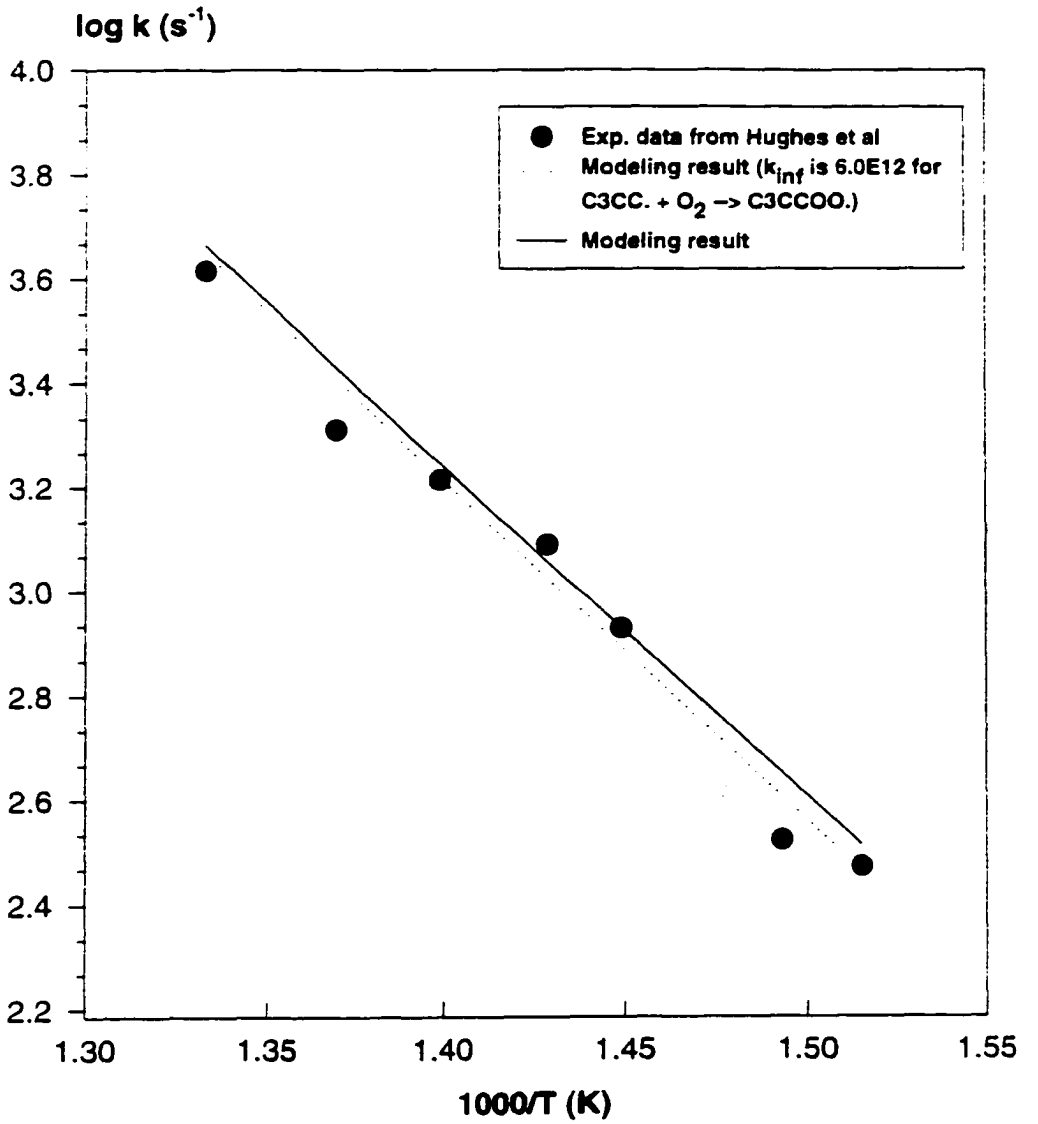
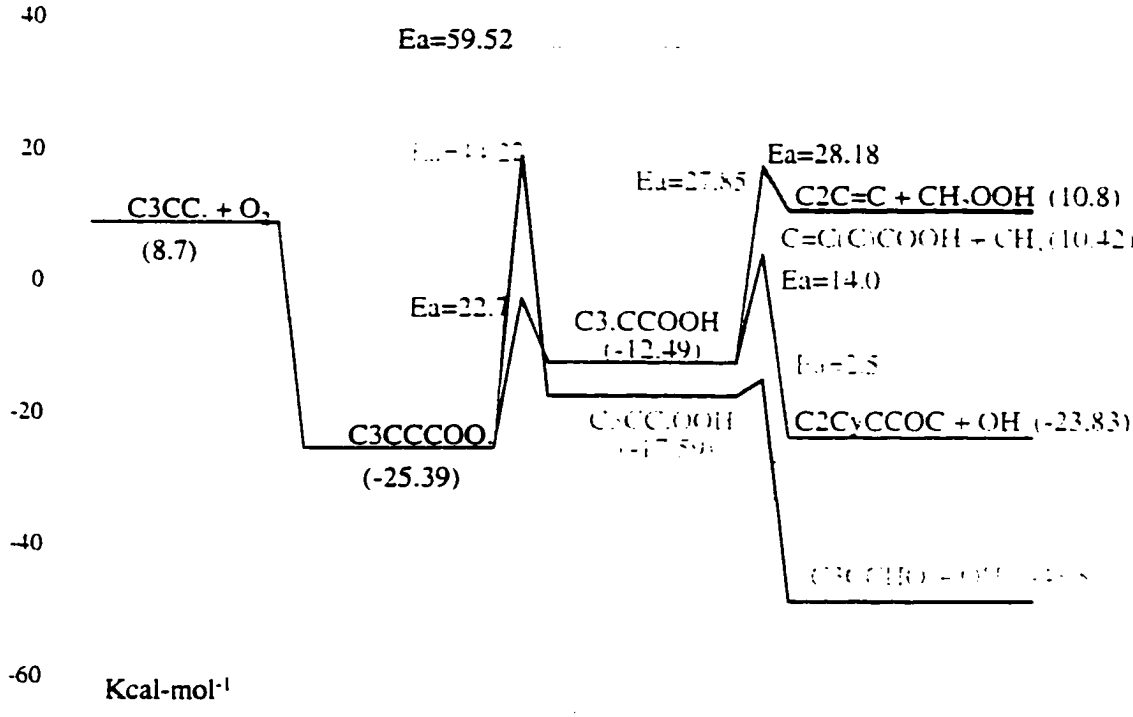


Figure IC. 21 Log k of OH formation vs 1000/T comparison of model with experiment

APPENDIX ID

QRRK INPUT PARAMETERS IN THE NEO-C_5H_{11} + O_2 SYSTEM

ID. 1 C3CC.+ O_2 → Products



	Reaction	A (s^{-1} or cm^3/mol-s)	n	Ea (kcal/mol)
k_1	C3CC + O_2→ C3CCOO.	1.00E12	0.00	0.00
k_{-1}	C3CCOO. → C3CC + O_2	2.27E14	0.00	31.68
k_2	C3CCOO. → C3.CCOOH	5.15E09	1.00	22.70
k_{-2}	C3.CCOOH → C3CCOO.	1.29E12	-0.74	8.90
k_3	C3.CCOOH → C2CyCCOC + OH	5.06E07	0.71	14.00
k_4	C3.CCOOH → C2C=C + CH_2OOH	5.23E13	0.00	28.18
k_5	C3.CCOOH → C=C(C)COOH + CH3	4.77E13	0.00	27.85
k_6	C3CCOO. → C3CC.OOH	2.60E10	1.00	44.22
k_{-6}	C3CC.OOH → C3CCOO.	7.50E12	-0.35	35.64
k_7	C3CC.OOH → C3CC=O + OH	1.43E13	0.00	2.50
k_8	C3CCOO. → C3CCO + O	1.03E15	0.00	59.52

frequency/degeneracy (CPFIT):
C3CCOO.: 952.2/45.5; C3.CCOOH: 898.2/45.0; C3CC.OOH: 880.6/45.0
Lennard-Jones parameter:
σ(a) = 5.86 ε/k (K) = 632

Beta values for QRRK calculations:

Temp.(K)	300	600	900	1200	1500	1800	2100	2400
Beta	0.117	0.018	0.004	0.004	0.008	0.011	0.014	0.016

k_1 A_1 = 1.0E12, take average value of high pressure limit data from Bayes et al.; $Ea_1 = 0$

k_{-1} Via k_1 and MR; $Ea_{-1} = Ea_1 + \Delta U_{rxn}$

k_2 A_2 estimated using TST, A = (deg.)(ek_b/h)exp($\Delta S^{\circ}(T)$/R), $\Delta S^{\circ}(T)$ is taken from MOPAC PM3 calculation, here ΔS°_{avg}(298., 1500. K) = -9.13 cal/mole-K, deg. = 9; Ea_2 = RS + E_{abst} + ΔH_{rxn}, 6 member ring (RS = 1), E_{abst} = 12.5 - (ΔH_{rxn}/3), ΔH_{rxn}=13.80 kcal./mole

k_{-2} Via k_2 and MR; $Ea_{-2} = Ea_2 - \Delta H_{rxn}$

k_3 A_3 estimated using TST, A = 5.66×10^{10}exp($\Delta S^{\circ}(T)$/R) in AT^nexp(-E_a/RT) form, $\Delta S^{\circ}(T)$ is taken from MOPAC PM3 calculation, here ΔS°_{avg}(298., 1500. K) = -13.95 cal/mole-K; Ea_3 estimated in this study

k_4 A_4 via A_{-4} (NIST), and MR; $Ea_4 = \Delta U_{rxn} + Ea_{-4}$

k_5 A_5 via A_{-5} (NIST), and MR; $Ea_5 = \Delta U_{rxn} + Ea_{-5}$

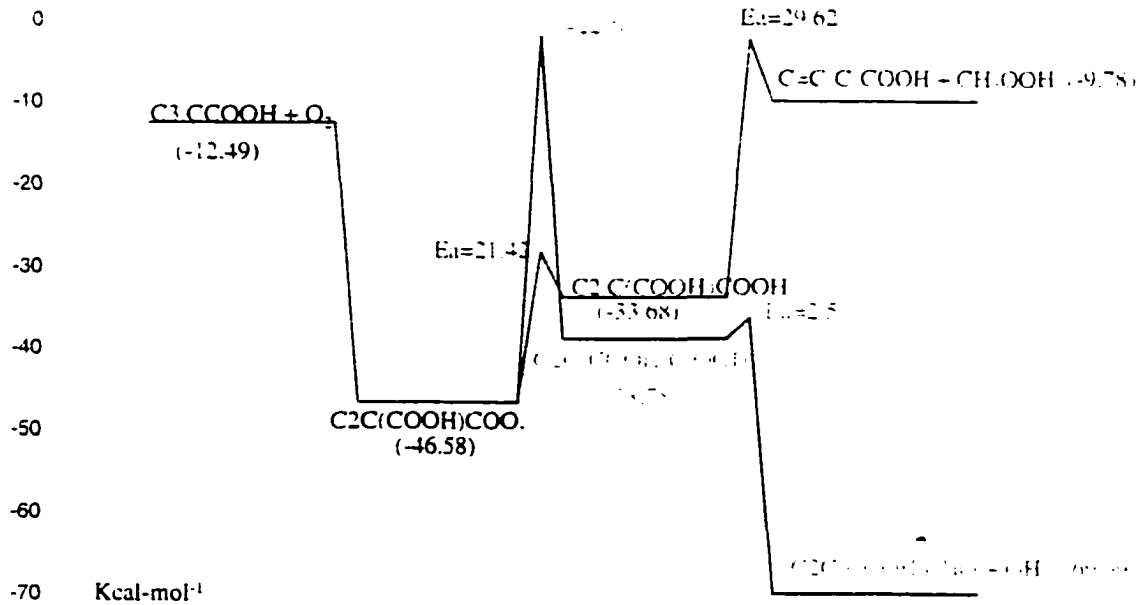
k_6 A_6 estimated using TST, loss of one rotors (4.3*1), gain of OI (Rln2), deg. = 2; Ea_6 = RS + E_{abst} + ΔH_{rxn}, 4 member ring (RS=26), E_{abst} = 12.5 + (ΔH_{rxn}/3), ΔH_{rxn} = 8.58

k_{-6} Via k_6 and MR; $Ea_{-6} = Ea_6 - \Delta H_{rxn}$

k_7 A_7 via A_{-7} which estimated from 1/2(OH + C=C), and MR; Ea_7 = 2.5 (NIST),

k_8 A_8 via A_{-8} (NIST)), and MR; $Ea_8 = 0.0$

ID. 2 C3.CCOOH + O_2 → Products



	Reaction	A (s^{-1} or cm^3/mol-s)	n	Ea (kcal/mol)
k_1	C3.CCOOH + O_2→ C2C(COOH)COO.	1.00E12	0.00	0.00
k_{-1}	C2C(COOH)COO. → C3.CCOOH + O_2	3.54E14	0.00	32.21
k_2	C2C(COOH)COO. → C2.C(COOH)COOH	1.03E09	1.00	21.42
k_{-2}	C2.C(COOH)COOH → C2C(COOH)COO.	1.10E10	0.12	8.04
k_3	C2.C(COOH)COOH → C=C(C)COOH + CH_2OOH	2.63E14	0.00	29.62
k_4	C2C(COOH)COO.→ C2C(COOH)C.OOH	2.60E10	1.00	44.56
k_{-4}	C2C(COOH)C.OOH → C2C(COOH)COO.	2.19E15	-1.39	35.47
k_5	C2C(COOH)C.OOH → C2C(COOH)C=O + OH	1.43E13	0.00	2.50

frequency/degeneracy (CPFIT):
C2C(COOH)COO.: 863.1/50.5; C2.C(COOH)COOH: 823.2/50.0;
C2C(COOH)C.OOH: 616.8/50.0
Lennard-Jones parameter:
σ(a) = 6.40 ε/k (K) = 720.5

Beta values for QRRK calculations for adduct C2C(COOH)COO.

Temp.(K)	300	600	900	1200	1500	1800	2100	2400
Beta	0.111	0.014	0.004	0.008	0.013	0.018	0.019	0.019

k_1 A_1 = 1.0E12, take average value of high pressure limit data from Bayes et al.: Ea_1 = 0.

k_{-1} Via k_1 and MR: $Ea_{-1} = Ea_1 + \Delta U_{rxn}$

k_2 A_2 estimated using TST, loss of three rotors (4.3*3), gain of OI (Rln2), deg. = 6: $Ea_2 = RS + E_{abst} + \Delta H_{rxn}$, 6 member ring (RS = 1), $E_{abst} = 12.5 + (\Delta H_{rxn}/3)$, ΔH_{rxn}= 13.38

k_{-2} Via k_2 and MR: $Ea_{-2} = Ea_2 - \Delta H_{rxn}$

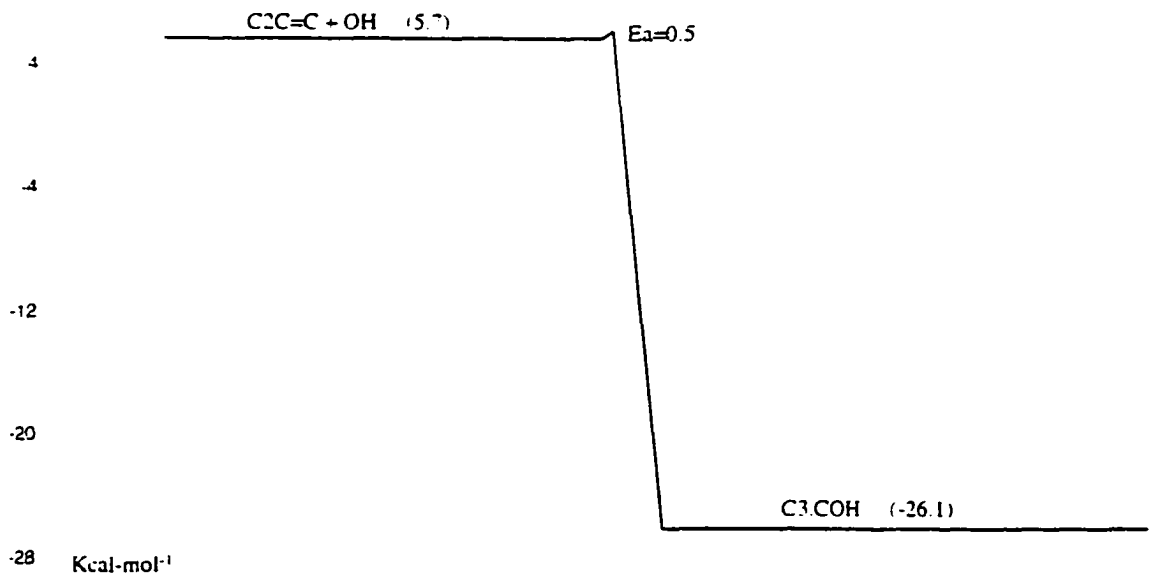
k_3 A_3 via A_{-3} = 1E11.2 (NIST), and MR: $Ea_3 = \Delta U_{rxn} + Ea_{-3}$, Ea_{-3} = 7.8, ΔU_{rxn} = 21.82

k_4 A_4 estimated using TST, loss of one rotors (4.3*1), gain of OI (Rln2), deg.= 2: $E_4 = RS + E_{abst} + \Delta H_{rxn}$, 4 member ring (RS = 26),$E_{abst} = 12.5 + (\Delta H_{rxn}/3)$ or 5, ΔH_{rxn} = 9.09

k_{-4} Via k_4 and MR: $Ea_{-4} = Ea_4 - \Delta H_{rxn}$

k_5 A_5 via A_{-5} = 2.75E12, estimated from 1/2 (OH + C=C), and MR: Ea_5 = 2.5

ID. 3 C2C=C + OH → Products

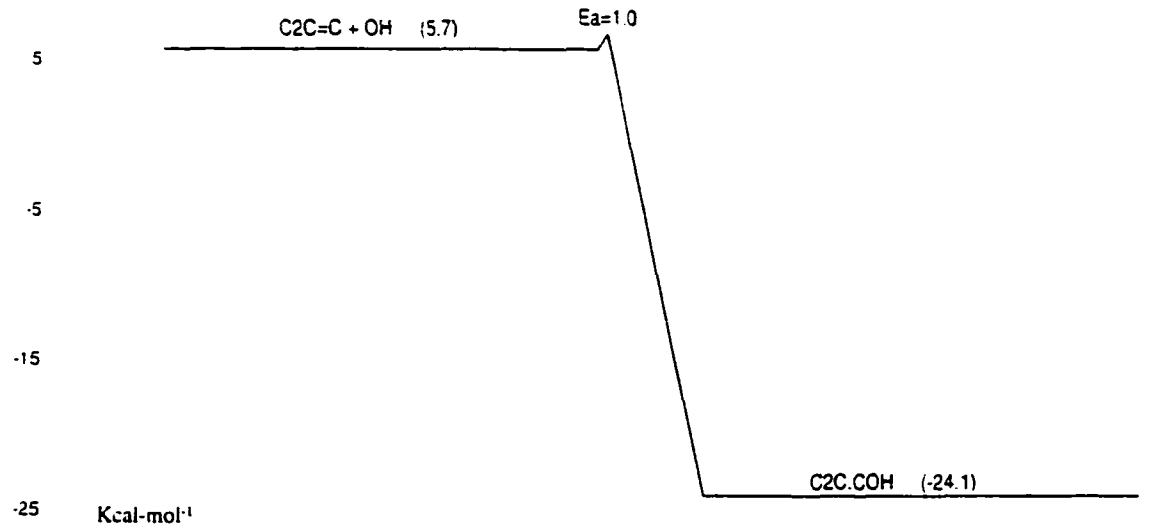


	Reaction	A (s^{-1} or cm^3/mol-s)	n	E_a (kcal/mol)
k_1	C2C=C + OH → C3.COH	2.92E12	0.0	0.5
k_{-1}	C3.COH → C2C=C + OH	4.22E13	0.0	31.95

frequency/degeneracy (CPFIT):
C3.COH: 1105.1/34.0
Lennard-Jones parameter:
σ(a) = 5.20 ε/k (K) = 533.1

k_1 A_1 = 2.92E12, estimated from (C_3H_6 + OH , 91 TSA), and MR; Ea_1 = 0.5 (NIST)
k_{-1} Via k_1 and MR; $Ea_{-1} = Ea_1 + \Delta U_{rxn}$

ID. 4 C2C=C + OH → C2C.COH

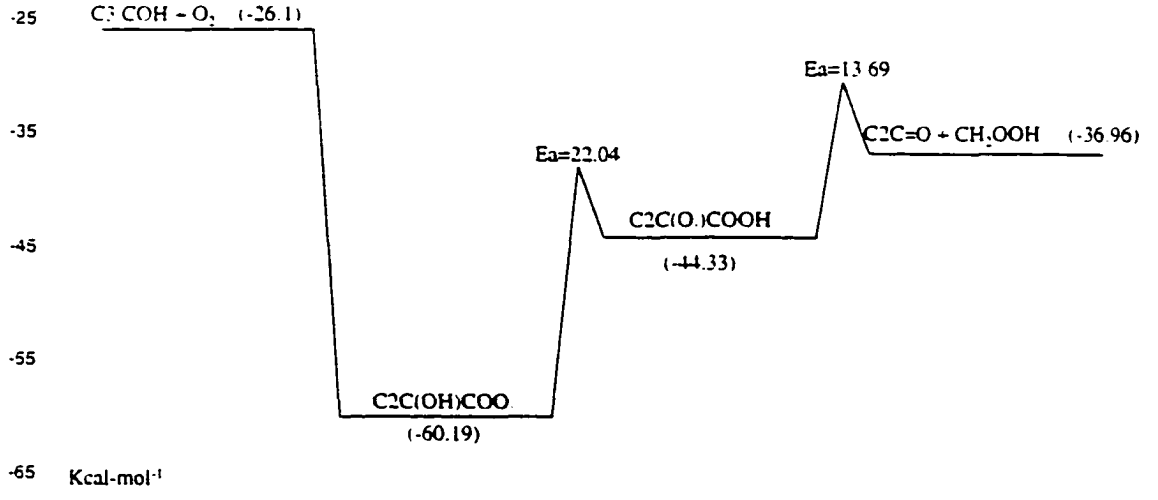


	Reaction	A (s^{-1} or cm^3/mol-s)	n	E_a (kcal/mol)
k_1	C2C=C + OH → C2C.COH	2.92E12	0.0	1.0
k_{-1}	C2C.COH → C2C=C + OH	1.95E13	0.0	31.51

frequency/degeneracy (CPFIT):
C2C.COH: 1153.5/34.0
Lennard-Jones parameter:
σ(a) = 5.20 ε/k (K) = 533.1

k_1 A_1 = 2.92E12, estimated from (C_3H_6 + OH , 91 TSA), and MR; E_1 = 1.0 (NIST)
k_{-1} Via k_1 and MR; $Ea_{-1} = Ea_1 + \Delta U_{rxn}$

ID. 5 C3.COH + O_2 → Products



	Reaction	A (s^{-1} or cm^3/mol-s)	n	Ea (kcal/mol)
k_1	C3.COH + O_2→ C2C(OH)COO.	2.0E12	0.0	0.00
k_{-1}	C2C(OH)COO. → C3.COH + O_2	4.589E14	0.0	31.71
k_2	C2C(OH)COO.→ C2C(O.)COOH	1.72E8	1.0	22.04
k_{-2}	C2C(O.)COOH → C2C(OH)COO.	1.73E11	-0.06	5.00
k_3	C2C(O.)COOH → C2C=O + CH_2OOH	3.492E14	0.0	13.69

frequency/degeneracy (CPFIT):
C2C(OH)COO.: 933.1/39.5; C2C(O.)COOH: 882.4/395
Lennard-Jones parameter:
σ(a) = 5.86 ε/k (K) = 632.1

k_1 A_1 = 2.0E12, estimated from R. + O_2 → ROO.; Ea_1 = 0.0

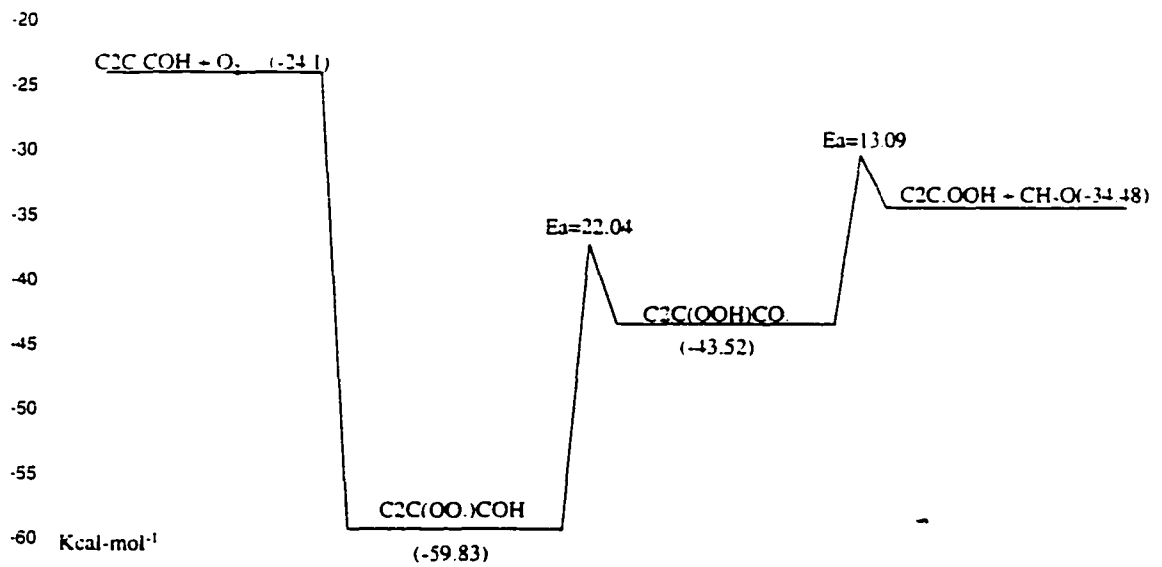
k_{-1} Via k_1 and MR; $Ea_{-1} = Ea_1 + \Delta U_{rxn}$

k_2 A_2 estimated using TST, loss of three rotors (4.3*3), gain of OI (Rln2), deg. = 1; Ea_2 = RS + E_{abst} + ΔH_{rxn}, 6 member ring (RS = 0), E_{abst} = 5 (NIST), ΔH_{rxn} = 17.04

k_{-2} Via k_2 and MR; $Ea_{-2} = Ea_2 - \Delta H_{rxn}$

k_3 A_3 via A_{-3} = 1E11.2 (NIST), and MR; $E_{a3} = \Delta H_{rxn} + Ea_{-3}$, Ea_{-3} = 7.8, ΔH_{rxn} = 5.89

ID. 6 C2C.COH + O_2 → Products



	Reaction	A (s^{-1} or cm^3/mol-s)	n	E_a (kcal/mol)
k_1	C2C.COH + O_2→ C2C(OO.)COH	2.0E12	0.0	0.0
k_{-1}	C2C(OO.)COH → C2C.COH + O_2	2.252E15	0.0	32.05
k_2	C2C(OO.)COH→ C2C(OOH)CO.	1.72E8	1.0	22.04
k_{-2}	C2C(OOH)CO.→ C2C(OO.)COH	1.71E11	-0.06	5.0
k_3	C2C(OOH)CO.→ C2C.OOH + HCHO	3.42E14	0.0	13.09

frequency/degeneracy (CPFIT):
C2C(OO.)COH: 955.2/39.5; C2C(OOH)CO.: 901.6/39.5
Lennard-Jones parameter:
σ(a) = 5.86 ε/k (K) = 632.1

k_1 A_1 = 2.0E12, estimated from R. + O_2 → ROO.; Ea_1 = 0.0

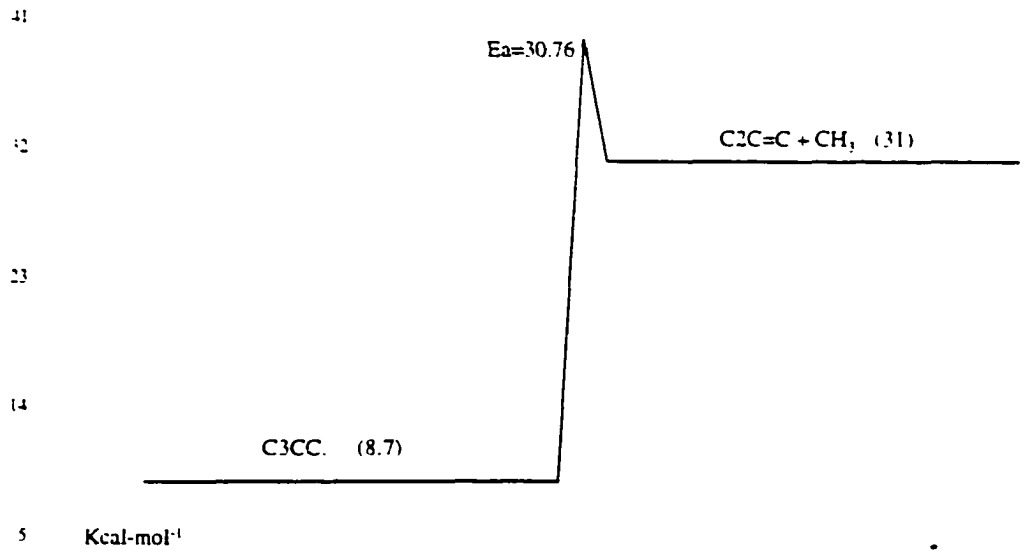
k_{-1} Via k_1 and MR; $Ea_{-1} = Ea_1 + \Delta U_{rxn}$

k_2 A_2 estimated using TST, loss of three rotors (4.3*3), gain of OI (Rln2), deg. = 1; Ea_2 = RS + E_{abst} + ΔH_{rxn}, 6 member ring (RS = 0), E_{abst} = 5 (NIST), ΔH_{rxn} = 17.04

k_{-2} Via k_2 and MR; $Ea_{-2} = Ea_2 - \Delta H_{rxn}$

k_3 A_3 via A_{-3} = 1E11.0 (NIST), and MR; $E_{a3} = \Delta H_{rxn} + Ea_{-3}$, Ea_{-3} = 5.9 which estimated from (CH_3 + CH_2O, 84 WAR),, ΔH_{rxn} = 7.19

ID. 7 C3CC. → C2C=C + CH_3

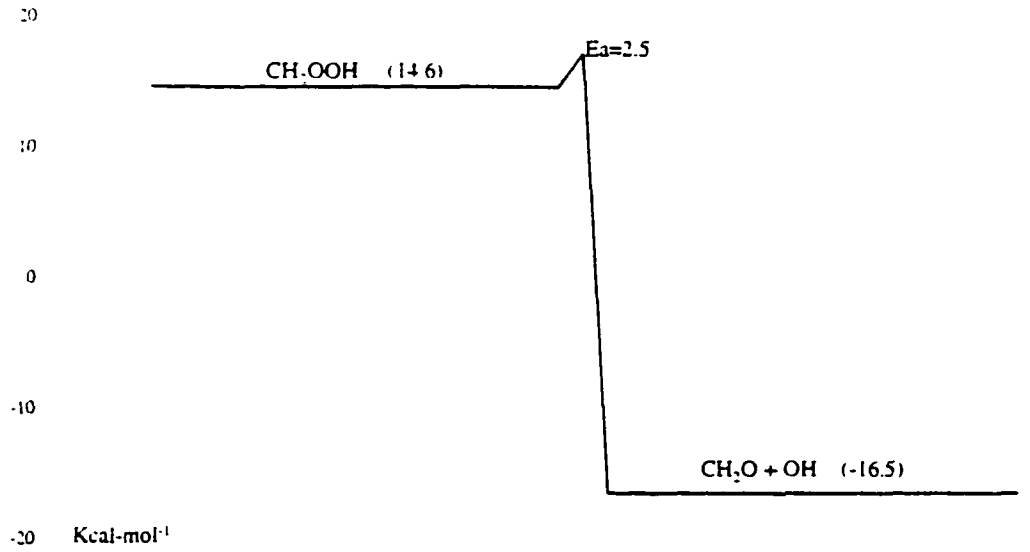


	Reaction	A(s^{-1})	n	E_a(kcal/mol)
k_1	C3CC. → C2C=C + CH_3	9.572E13		30.76

frequency/degeneracy (CPFIT):
C3CC.: 1123.5/40.0
Lennard-Jones parameter:
σ(a) = 5.50 ε/k (K) = 443

k_1 A_1 via A_{-1} (1E11.5), estimated by NIST, and MR; $Ea_1 = Ea_{-1} + \Delta H_{rxn}$, Ea_{-1} = 7.8, ΔH_{rxn} = 21.03

ID. 8 $CH_2OOH \rightarrow CH_2O + OH$

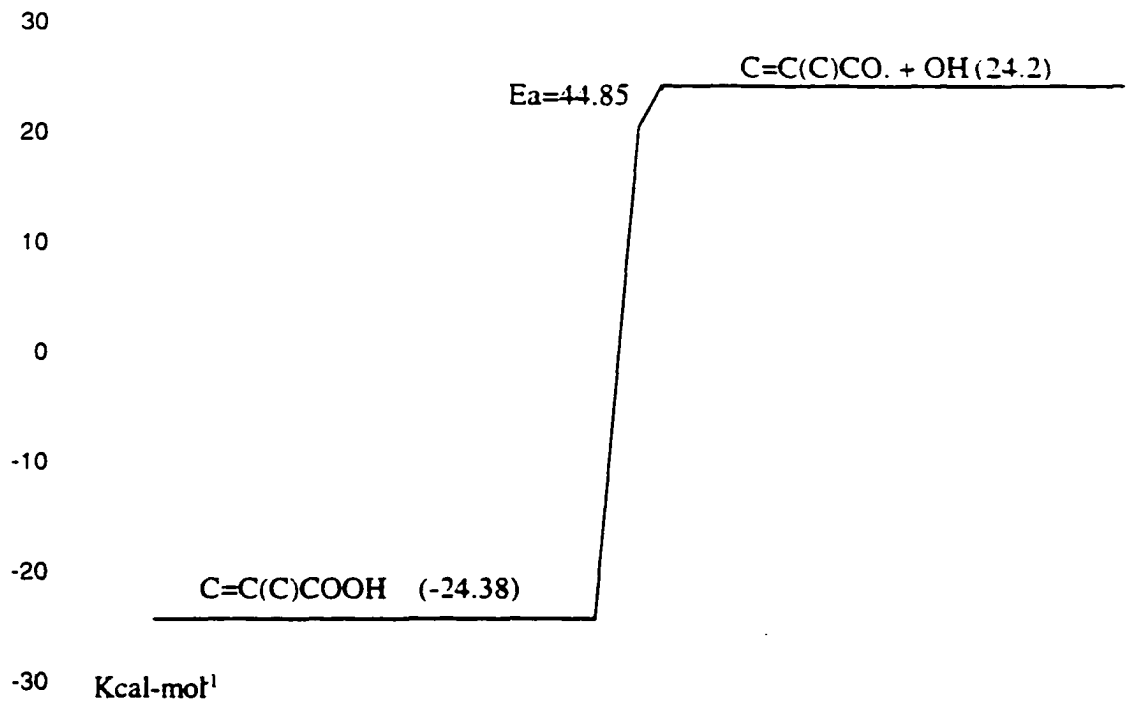


	Reaction	A(s^{-1})	n	E_a(kcal/mol)
k_1	$CH_2OOH \rightarrow HCHO + OH$	3.069E12	0.0	2.5

frequency/degeneracy (CPFIT):
CH_2OOH: 613.7/11.0
Lennard-Jones parameter:
σ(a) = 4.34 ε/k (K) = 432

k_1 A_1 via A_{-1} which estimated from 1/2 (OH + C=C), and MR. Ea_1 = 2.5 (NIST)

ID. 9 C=C(C)COOH → C=C(C)CO. + OH

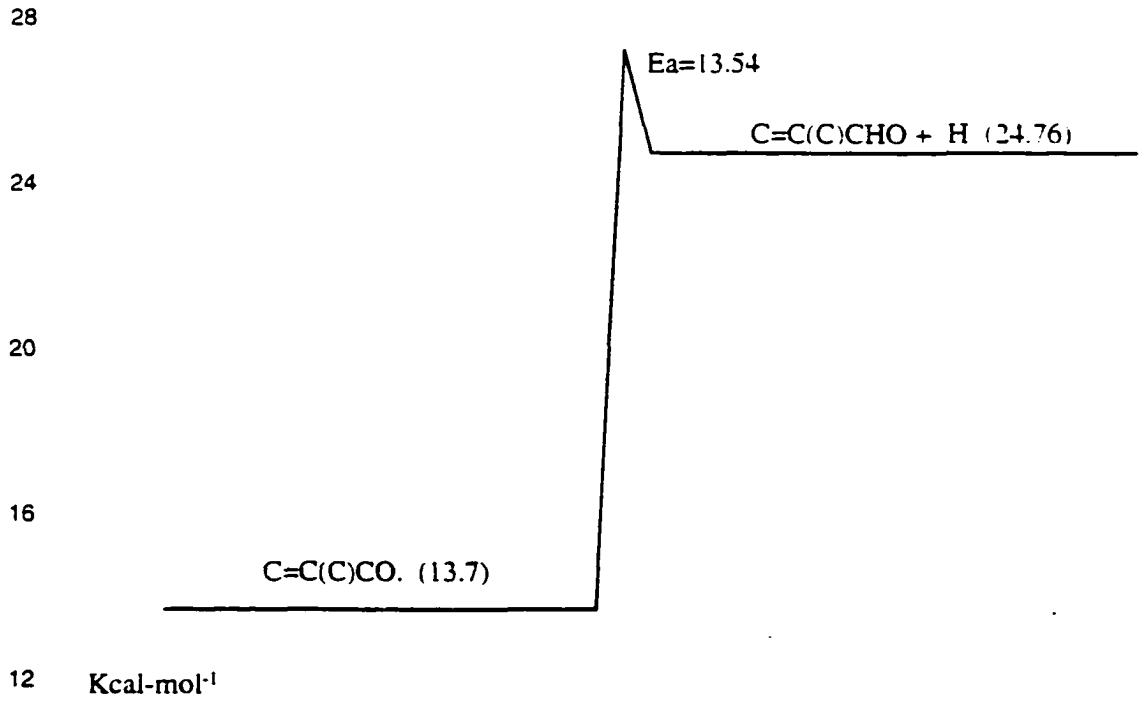


	Reaction	A(s^{-1})	n	E_a(kcal/mol)
k_1	C=C(C)COOH → C=C(C)CO. + OH	2.21E15	0.0	44.85

frequency/degeneracy (CPFIT):
C=C(C)COOH: 898.2/34.0
Lennard-Jones parameter:
σ(a) = 5.55 ε/k (K) = 584.9

k_1 Via k_{-1} estimated from (n-C_3H_7 + OH = n-C_3H_7OH, 88 TSA), and MR

ID. 10 C=C(C)CO. → C=C(C)CHO + H

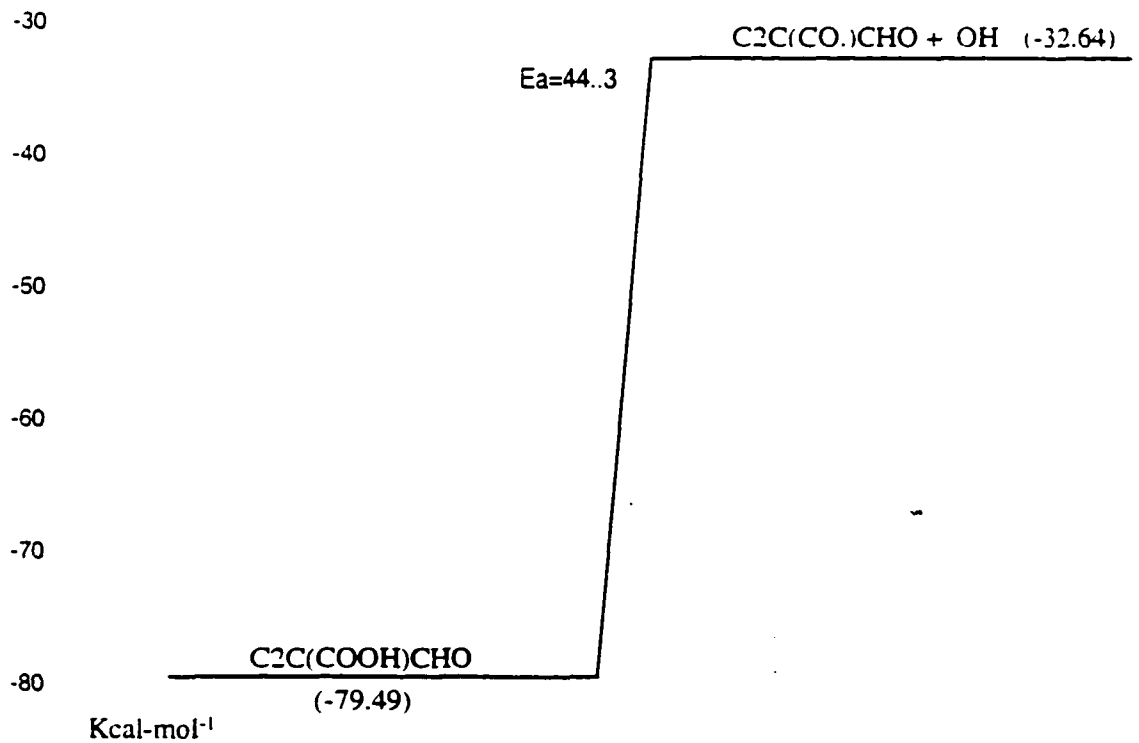


	Reaction	A(s^{-1})	n	E_a(kcal/mol)
k_1	C=C(C)CO. → C=C(C)C=O. + H	4.175e12	0.0	13.54

frequency/degeneracy (CPFIT):
C=C(C)CO.: 1110.9/29.0
Lennard-Jones parameter:
σ(a) = 5.20 ε/k (K) = 533.1

k_1 A_1 via A_{-1} = 5E12 which estimated from 1/2(C_2H_4 + H , 91 TSA), and MR; $Ea_1 = Ea_{-1} + \Delta H_{rxn}$, ΔH_{rxn} = 12.63, Ea_{-1} = 2.7 (NIST)

ID. 11 C2C(COOH)CHO → C2C(CO.)CHO + OH

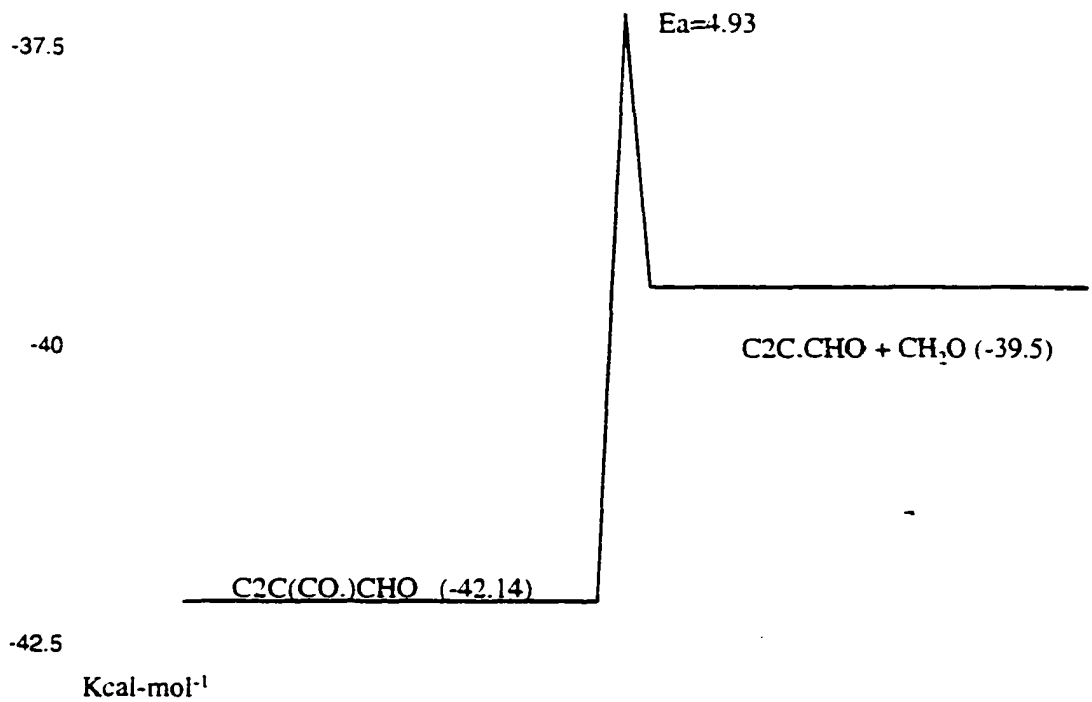


	Reaction	A (s^{-1})	n	E_a(kcal/mol)
k_1	C2C(COOH)C=O → C2C(CO.)C=O + OH	3.222E15	0.0	44.30

frequency/degeneracy (CPFIT):
C2C(COOH)C=O: 857.1/45.0
Lennard-Jones parameter:
σ(a) = 6.14 ε/k (K) = 678.6

k_1 Via k_{-1} estimated from (n-C_3H_7 + OH = n-C_3H_7OH, 88 TSA), and MR

ID. 12 C2C(CO.)CHO → C2C.CHO + CH_2O

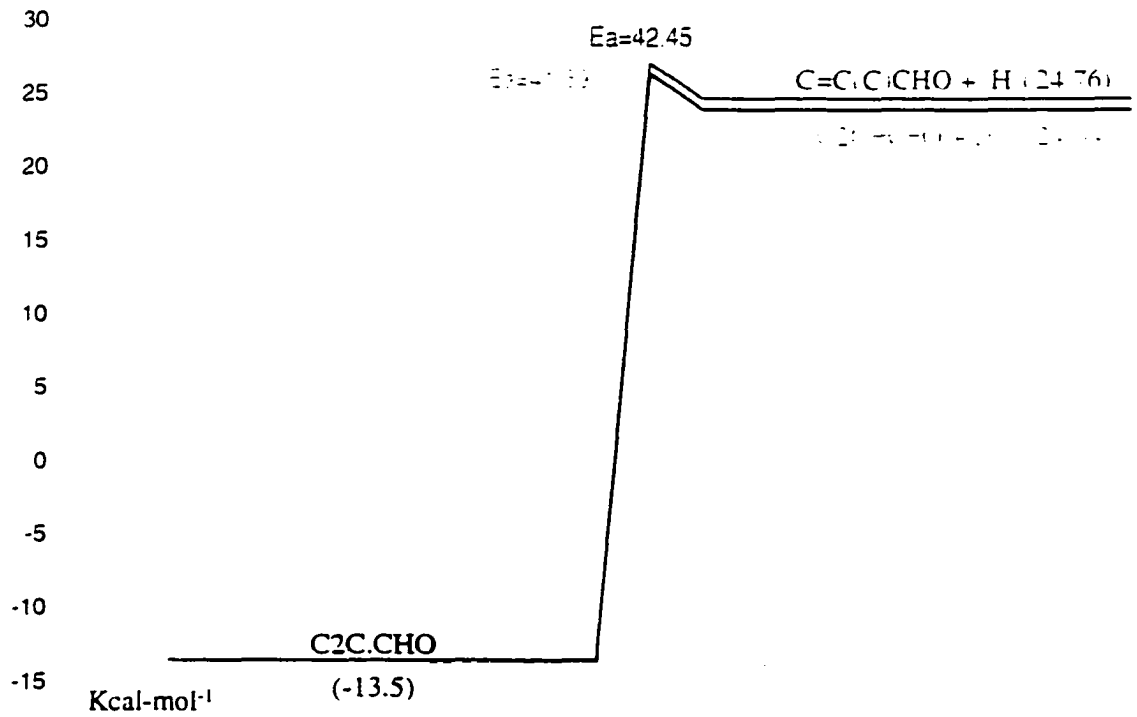


	Reaction	A(s^{-1})	n	E_a(kcal/mol)
k_1	C2C(CO.)C=O → C2C.C=O + HCHO	7.295E12	0.0	4.932

frequency/degeneracy (CPFIT):
C2C(CO.)C=O: 1010.9/40.0
Lennard-Jones parameter:
σ(a) = 5.86 ε/k (K) = 632.7

k_1 Via k_{-1} estimated from (HCHO + CH_3 , 84 WAR), and MR

ID. 13 C2C.CHO → Products



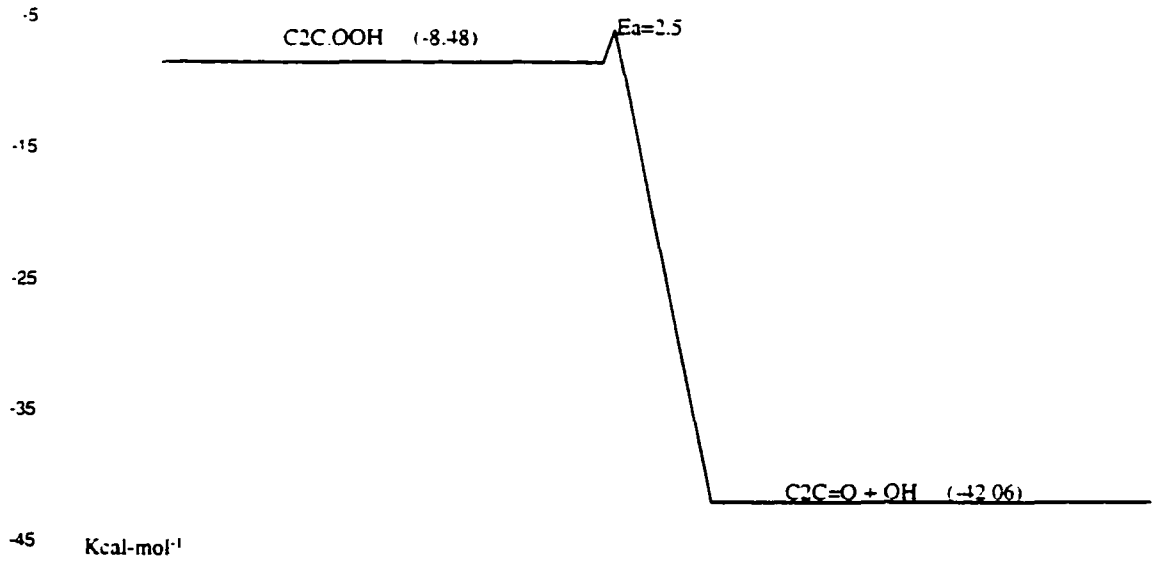
	Reaction	A(s^{-1})	n	E_a(kcal/mol)
k_1	C2C.C=O → C=C(C)C=O + H	1.442E13	0	42.45
k_2	C2C.C=O → C2C=C=O + H	1.076E13	0	41.69

frequency/degeneracy (CPFIT):
C2C.C=O: 1047.8/28.5
Lennard-Jones parameter:
σ(a) = 5.20 ε/k (K) = 533.1

k_1 A_1 via A_{-1} = 5E12 which estimated from 1/2(C_2H_4 + H, 91 TSA), and MR; Ea_1 = Ea_{-1} + ΔH_{rxn}, ΔH_{rxn} = 39.75, Ea_{-1} = 2.7 (NIST)

k_2 A_2 via A_{-2} = 5E12 which estimated from 1/2(C_2H_4 + H, 91 TSA), and MR; Ea_2 = Ea_{-2} + ΔH_{rxn}, ΔH_{rxn} = 38.99, Ea_{-1} = 2.7 (NIST)

ID. 14 C2C.OOH → C2C=O + OH



	Reaction	A(s^{-1})	n	E_a(kcal/mol)
k_1	C2C.OOH → C2C=O + OH	4.485E12	0.0	2.5

frequency/degeneracy (CPFIT):
C2C.OOH: 750.2/28.0
Lennard-Jones parameter:
σ(a) = 5.20 ε/k (K) = 533.1

k_1 A_1 via A_{-1} = 2.75E12 which estimated from 1/2(C=C + OH), and MR; Ea_1 = 2.5 (NIST)

APPENDIX IIA

TABLES IN MTBE SYSTEM

Table IIA. 1 Experimental Conditions of MTBE Oxidation and Pyrolysis

4 atm		7 atm		10 atm	
Temp. (°C)	RT (second)	Temp. (°C)	RT (second)	Temp. (°C)	RT (second)
MTBE Oxidation At φ = 0.75					
750	0.45-0.90	750	0.80-2.90	750	1.00-4.90
700	0.45-1.00	700	0.80-3.10	700	1.10-5.10
650	0.50-0.90	650	0.90-3.30	650	1.10-5.30
625	0.50-1.10	600	0.80-3.50	600	1.70-5.70
600	0.55-1.10	550	1.00-3.40	550	1.30-5.70
575	0.60-1.10	525	1.00-3.80	525	1.60-5.80
550	0.60-1.20				
MTBE Oxidation At φ = 1.00					
800	0.3-0.9	800	0.7-2.7	800	0.9-4.7
750	0.45-0.9	750	0.8-2.9	750	1-4.9
700	0.45-1.0	700	0.8-3.1	700	1.1-5.1
650	0.5-1.0	650	0.9-3.3	650	1.3-5.5
600	0.55-1.1	600	0.9-3.5	600	1.3-5.7
575	0.6-1.1	550	1-3.4	550	1.3-5.7
550	0.6-1.2	525	1-3.8	525	1.4-6.2
MTBE Oxidation At φ = 1.50					
775	0.5-0.9	775	0.8-2.8	775	1-3.6
725	0.5-1.0	725	0.8-3	725	1.2-5.2
700	0.45-1.0	700	0.8-3.1	700	1.1-5.1
650	0.5-1.0	650	0.9-3.3	650	1.3-5.5
625	0.5-1.1	625	1-3.4	625	1.3-4.5
600	0.55-1.1	600	0.9-3.5	600	1.3-5.7
575	0.6-1.1	575	1-3.4	575	1.4-6.2
550	0.6-1.2	550	1-3.4	550	1.3-5.7
		525	1-3.8	525	1.4-6.2
MTBE Pyrolysis					
850	0.45-0.85	850	0.8-2.6	850	1-3.6
800	0.3-0.9	800	0.7-2.7	800	1-4.9
775	0.5-0.9	775	0.8-2.8	775	1-3.6
750	0.45-0.9	750	0.8-2.9	750	1-4.9
725	0.5-1.0	725	0.8-3	725	1.2-5.2
700	0.45-1.0	700	0.8--3.1	700	1.1-5.5
650	0.5-1.0	650	0.9-3.3	650	1.1-5.7
600	0.55-1.1	600	1-3.5	600	1.3-5.7
550	0.6-1.2				

Table IIA. 2 Retention Time of Species

Species	RT (A) (min)	RRF (A)	RT (B) (min)	RRF (B)
CO	1.01	0.906		
CH_4	1.28	1.000	3.18	1.000
CO_2	3.24	0.906		
C_2H_4	4.53	1.591	3.27	1.740
C_2H_6	5.64	1.975	3.30	1.798
C_2H_2	6.87	0.777	3.27	1.744
CH_2O	10.70	0.864	3.50	<0.1
C_3H_6	11.39	2.479	3.55	2.656
C_3H_8	11.62	2.938	3.55	2.747
C_3H_4	12.92	1.387	3.76	2.488
CH_3OCH_3	13.01		3.90	
CH_3OH	14.55	1.075	4.15	0.784
CH3CHO	14.85		4.27	
$(CH_3)_3CH$	15.31	4.15	3.81	4.061
$CH_2=CHCH_2CH_3$	15.77	3.129	4.21	3.476
CCCC	16.03	3.924	4.27	3.714
$(CH_3)_4C$	18.36	5.073	4.28	5.325
C=CCHO	19.70	2.962	6.15	1.807
C_2CCC	20.54	5.2	5.25	5.097
C=CCCC	21.05	4.242	5.76	4.481
$C_2C=O$	21.07	3.00	6.30	1.654
CCCCC	21.55	4.822	5.91	4.583
COCOC	21.90	3.097	6.83	1.324
C=C(C)CHO	27.80	3.150	8.40	2.058
C2CCHO	28.20	3.690	8.10	3.128
CCC(C)CC	28.54	5.36	6.65	5.850
MTBE (C_3COC)	30.778	5.472	8.12	3.830
C_3CCC	31.741	5.378	7.57	5.929
C_2CCCC	32.928	5.4	8.03	6.000
C=CCCCC	33.867	4.708	8.42	5.583
CCCCCC	34.826	5.585	8.61	5.350

Table IIA. 3 Thermodynamic Properties for Species in MTBE Model

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE		ELEME	N	TS			
AR	0.00	36.98	4.97	4.97	4.97	4.97	4.97	4.97	4.97		7/12/93		0	0	0 AR	1 G	0
HE	0.00	30.12	4.97	4.97	4.97	4.97	4.97	4.97	4.97			HE	1	0	0	0 G	0
I	25.50	43.20	5.00	5.00	5.00	5.00	5.00	5.00	5.00	BENSON		I	1	0	0	0 G	0
N2	0.00	45.70	6.67	6.83	6.97	7.11	7.36	7.57	7.99	Xi		N	2	0	0	0 G	0
O	59.51	38.40	5.00	5.00	5.00	5.00	5.00	5.00	5.00		120186	O	1	0	0	0 G	0
X	59.51	38.40	5.00	5.00	5.00	5.00	5.00	5.00	5.00		120186	O	1	0	0	0 G	0
O2	0.00	49.00	6.86	7.10	7.33	7.54	7.89	8.18	8.70			O	2	0	0	0 G	0
H	52.10	27.30	4.90	4.90	4.90	4.90	4.90	4.90	4.90			H	1	0	0	0 G	0
OH	9.50	43.80	6.79	6.86	6.93	7.00	7.14	7.28	0.00			H	1 O	1	0	0 G	0
Y	9.50	43.80	6.79	6.86	6.93	7.00	7.14	7.28	0.00			H	1 O	1	0	0 G	0
HO2	3.50	54.73	8.37	8.95	9.48	9.96	10.78	11.43	12.47	JANAF		H	1 O	2	0	0 G	0
H2	0.00	31.20	6.89	6.97	7.05	7.12	7.27	7.41	7.69			H	2	0	0	0 G	0
H2O	-57.80	45.10	8.02	8.19	8.41	8.66	9.24	9.85	11.23	BSN		H	2 O	1	0	0 G	0
H2O2	-32.60	55.70	10.53	11.76	12.74	13.50	14.58	15.29	16.50	5/7/91	THERM	H	2 O	2	0	0 G	1
C	170.88	38.31	4.98	4.97	4.97	4.97	4.97	4.97	4.97	J 3/61		C	1	0	0	0 G	0
C(S)	0.00	21.83	2.06	2.86	3.50	4.02	4.73	5.16	5.65	J 3/61		C	1	0	0	0 G	0
CO	-26.40	47.20	6.71	6.89	7.06	7.23	7.53	7.79	8.29		121286	C	1 O	1	0	0 G	0
CO2	-94.01	51.00	8.90	9.81	10.57	11.20	12.17	12.84	13.77		121286	C	1 O	2	0	0 G	0
CH	142.00	43.72	6.97	6.97	7.03	7.12	7.41	7.77	8.74	J12/67		C	1 H	1	0	0 G	0
CHO	10.90	53.42	7.64	7.95	8.50	9.10	10.21	11.08	0.00		10/31/96	C	1 H	1 O	1	0 G	0
O.C*O	-38.30	65.04	9.52	11.00	12.30	13.29	15.12	16.26	0.00		10/31/96	C	1 H	1 O	2	0 G	0
HCO2.	-38.30	65.04	9.52	11.00	12.30	13.29	15.12	16.26	0.00		12/31/96	C	1 H	1 O	2	0 G	0
C.O2H	-35.80	66.11	10.87	12.14	13.17	13.94	15.47	16.42	0.00		1/7/97	C	1 H	1 O	2	0 G	1
HCQ.*O	-31.30	74.08	13.22	14.83	16.12	17.17	19.11	20.51	0.00	12/31/96	THERM	C	1 H	1 O	3	0 G	1
C.Q*O	-30.50	74.98	14.44	16.24	17.71	18.84	20.67	21.75	0.00	12/31/96	THERM	C	1 H	1 O	3	0 G	2
CH2S	101.45	44.15	8.33	8.77	9.21	9.64	10.45	11.16	12.47	K		C	1 H	2	0	0 G	0
CH2	92.36	46.32	8.33	8.77	9.21	9.64	10.45	11.16	12.47	K		C	1 H	2	0	0 G	0
HCHO	-26.00	50.92	8.47	9.38	10.46	11.52	13.37	14.81	0.00		10/31/96	C	1 H	2 O	1	0 G	0
HCOHT	48.36	60.95	10.79	11.97	12.81	13.58	14.84	15.81	17.26		10/9/95	C	1 H	2 O	1	0 G	1
HCOH	22.56	58.19	10.79	11.97	12.81	13.58	14.84	15.81	17.26		10/9/95	C	1 H	2 O	1	0 G	1

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS			
OC*O	-90.20	64.25	10.83	12.87	14.62	15.98	18.40	20.00	0.00	10/31/96	C	1	H	2	O	2 0 G 1
HCO2H	-90.20	64.25	10.83	12.87	14.62	15.98	18.40	20.00	0.00	12/30/96 THERM	C	1	H	2	O	2 0 G 1
HOC.HO.	2.83	65.50	13.45	14.35	15.26	16.25	18.06	19.37	0.00	1/2/97	C	1	H	2	O	2 0 G 1
HCQ*O	-67.40	73.86	15.27	17.67	19.67	21.26	23.83	25.48	0.00	12/31/96 THERM	C	1	H	2	O	3 0 G 2
C.(OH)2O.	-42.27	78.15	15.69	16.27	17.20	18.44	20.87	22.55	0.00	1/2/97	C	1	H	2	O	3 0 G 2
HOCHO.O.	-31.01	72.22	15.48	16.90	18.41	19.96	22.61	24.28	0.00	1/2/97	C	1	H	2	O	3 0 G 1
HOC.HQ.	1.54	74.82	17.19	18.34	19.27	20.32	22.17	24.00	0.00	1/2/97	C	1	H	2	O	3 0 G 2
HOC.HQ.T	-13.00	77.58	17.19	18.34	19.27	20.32	22.17	24.00	0.00	1/2/97	C	1	H	2	O	3 0 G 2
O.C.HQ	17.40	73.14	18.26	19.88	21.21	22.52	24.51	26.17	0.00	1/2/97	C	1	H	2	O	3 0 G 2
O.C.HQT	4.86	76.52	18.26	19.88	21.21	22.52	24.51	26.17	0.00	1/2/97	C	1	H	2	O	3 0 G 2
CH3	34.80	46.30	9.12	9.91	10.68	11.41	12.75	13.90	16.00	J 6/69	C	1	H	3		0 0 G 0
CH2OH	-3.60	59.03	11.77	13.27	14.42	15.47	17.22	18.61	20.85	10/31/96	C	1	H	3	O	1 0 G 1
CH3O	3.96	54.87	9.01	10.77	12.44	14.02	16.61	18.55	21.42	1/ 3/97 THERM	C	1	H	3	O	1 0 G 0
CH2OOH	14.60	68.25	16.55	18.40	19.87	21.44	23.20	24.93	0.00	10/31/96	C	1	H	3	O	2 0 G 2
CH3OO	4.30	65.18	13.88	15.47	16.85	18.44	20.49	22.71	0.00	10/31/96	C	1	H	3	O	2 0 G 1
HOCH2O.	-39.07	66.10	13.12	14.65	16.28	17.92	20.73	22.76	0.00	1/2/97	C	1	H	3	O	2 0 G 1
C.H(OH)2	-49.13	68.34	14.43	15.65	16.87	18.14	20.44	22.17	0.00	1/2/97	C	1	H	3	O	2 0 G 2
C.(OH)3	-94.23	79.61	16.67	17.57	18.81	20.33	23.25	25.35	0.00	1/2/97	C	1	H	3	O	3 0 G 3
CH(OH)2O.	-82.97	73.68	16.46	18.20	20.02	21.85	24.99	27.08	0.00	1/2/97	C	1	H	3	O	3 0 G 2
HOC.HQ	-34.56	77.36	19.24	21.18	22.82	24.41	26.89	28.97	0.00	1/2/97	C	1	H	3	O	3 0 G 3
CQH2O.	-24.50	75.12	17.93	20.18	22.23	24.19	27.18	29.56	0.00	1/2/97	C	1	H	3	O	3 0 G 2
CQ.H2OH	-40.36	76.80	16.86	18.64	20.29	21.99	24.84	27.39	0.00	1/2/97	C	1	H	3	O	3 0 G 2
CH2OHOO	-30.30	81.70	19.68	21.49	23.31	24.97	27.72	29.82	33.11	rayez,lev 11/	C	1	H	3	O	3 0 G 2
CH4	-17.90	44.40	8.71	9.82	10.99	12.19	14.52	16.60	20.17	J 3/61	C	1	H	4		0 0 G 0
CH3OH	-48.00	57.30	10.49	12.34	14.22	16.02	19.05	21.38	25.02	10/31/96	C	1	H	4	O	1 0 G 1
CH3OOH	-31.80	64.96	15.93	18.31	20.40	22.53	25.21	27.68	0.00	10/31/96	C	1	H	4	O	2 0 G 2
CH2(OH)2	-91.03	66.18	14.10	15.95	17.89	19.81	23.11	25.56	0.00	1/2/97	C	1	H	4	O	2 0 G 2
CH(OH)3	-134.93	75.14	17.44	19.50	21.63	23.74	27.37	29.88	0.00	1/2/97	C	1	H	4	O	3 0 G 3
CQH2OH	-76.46	76.58	18.91	21.48	23.84	26.08	29.56	32.36	0.00	1/2/97	C	1	H	4	O	3 0 G 3
C2H	134.46	51.51	10.05	10.42	10.71	10.96	11.47	11.95	12.92	10/31/96	C	2	H	1		0 0 G 0
C#CO.	56.33	57.60	11.88	12.79	13.68	14.94	16.02	16.97	0.00	1/ 2/97 THERM	C	2	H	1	O	1 0 G 0

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS				
C.#COH	101.03	60.82	12.71	13.22	13.89	14.95	15.68	16.33	0.00	1/ 2/97 THERM	C	2	H	1	O	1	0 G 1
C.*C*O	41.36	60.49	12.25	13.60	15.09	15.65	16.52	17.38	0.00	1/2/97	C	2	H	1	O	1	0 G 0
O*CC.*O	-19.70	65.41	14.71	16.69	18.05	19.19	21.07	21.91	0.00	1/ 2/97 THERM	C	2	H	1	O	2	0 G 1
C2H2	53.86	48.02	10.56	11.98	12.98	13.74	14.94	15.92	17.70	10/31/96	C	2	H	2		0	0 G 0
C*C*O	-11.74	56.45	12.70	14.65	16.73	17.80	19.50	20.98	23.03	10/31/96	C	2	H	2	O	1	0 G 0
C#COH	20.43	58.71	13.22	14.78	16.16	17.73	19.15	20.30	0.00	1/ 2/97 THERM	C	2	H	2	O	1	0 G 1
O*CC*O	-50.60	65.42	14.90	17.54	19.64	21.40	24.28	25.80	0.00	1/ 2/97 THERM	C	2	H	2	O	2	0 G 1
C2H3	71.62	55.23	10.01	11.97	13.66	15.08	17.32	19.05	21.85	10/31/96	C	2	H	3		0	0 G 0
CH3C.*O	-2.28	64.25	12.39	14.28	16.26	18.05	21.06	23.24	0.00	10/31/96	C	2	H	3	O	1	0 G 1
C*CO.	6.29	60.42	12.81	15.33	17.49	19.29	22.06	24.11	27.30	1/ 2/97 THERM	C	2	H	3	O	1	0 G 0
C.*COH	29.49	64.30	13.96	16.57	18.61	20.16	22.37	23.95	26.56	1/ 2/97 THERM	C	2	H	3	O	1	0 G 1
C*C.OH	24.79	63.39	14.19	16.59	18.52	20.04	22.26	23.86	26.51	1/ 2/97 THERM	C	2	H	3	O	1	0 G 1
CYC.OC	29.32	61.23	11.75	14.62	17.10	19.10	22.07	24.19	0.00	1/ 2/97 THERM	C	2	H	3	O	1	0 G 0
C.CHO	3.12	60.40	12.92	15.31	17.44	19.24	22.10	24.12	0.00	1/2/97	C	2	H	3	O	1	0 G 1
C*CQ.	28.50	69.96	16.35	19.17	21.54	23.49	26.52	28.77	0.00	1/ 2/97 THERM	C	2	H	3	O	2	0 G 1
C*C.Q	49.30	71.55	18.06	20.80	23.15	25.06	27.90	29.83	0.00	1/ 2/97 THERM	C	2	H	3	O	2	0 G 2
C.*CQ	51.50	72.51	18.21	21.26	23.73	25.66	28.42	30.25	0.00	1/ 2/97 THERM	C	2	H	3	O	2	0 G 2
O*CCO.	-21.54	72.11	16.55	18.77	20.73	22.52	25.94	28.21	0.00	1/ 2/97 THERM	C	2	H	3	O	2	0 G 1
O*CC.OH	-34.60	67.38	15.54	18.62	21.25	23.40	26.66	29.00	0.00	1/ 2/97 THERM	C	2	H	3	O	2	0 G 2
O*C.COH	-36.60	74.69	16.70	18.64	20.38	21.99	25.16	27.28	0.00	1/ 2/97 THERM	C	2	H	3	O	2	0 G 2
CYC.OOC	41.61	65.24	13.99	18.16	21.83	24.57	28.22	31.21	0.00	1/ 2/97 THERM	C	2	H	3	O	2	0 G 0
C2H4	12.52	52.47	10.20	12.72	15.02	17.00	20.14	22.54	26.38	10/31/96	C	2	H	4		0	0 G 0
CH3CHO	-39.18	63.13	13.22	15.71	18.22	20.47	24.22	26.97	0.00	10/31/96	C	2	H	4	O	1	0 G 1
C*COH	-29.61	61.53	14.15	17.32	19.97	22.08	25.19	27.44	31.09	1/ 2/97 THERM	C	2	H	4	O	1	0 G 1
CYCOC	-12.58	58.14	11.58	15.09	18.25	20.85	24.78	27.60	0.00	1/ 2/97 THERM	C	2	H	4	O	1	0 G 0
C*CQ	-7.60	69.74	18.40	22.01	25.09	27.58	31.24	33.74	0.00	1/ 2/97 THERM	C	2	H	4	O	2	0 G 2
O*CCOH	-73.50	73.57	17.53	20.07	22.34	24.41	28.32	31.01	0.00	1/ 2/97 THERM	C	2	H	4	O	2	0 G 2
CYCOOC	-2.29	60.77	14.05	18.68	22.94	26.31	31.07	34.90	0.00	1/ 2/97 THERM	C	2	H	4	O	2	0 G 0
CQCHO	-58.93	82.59	22.34	25.60	28.29	30.68	34.77	37.81	0.00	2/ 9/97 THERM	C	2	H	4	O	3	0 G 3
C2H5	28.60	59.87	11.61	14.32	16.89	19.18	22.88	25.80	30.50	10/31/96	C	2	H	5		0	0 G 1
CCO.	-4.24	65.64	14.50	17.89	20.91	23.56	27.77	30.91	0.00	1/ 2/97 THERM	C	2	H	5	O	1	0 G 1

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS		
C.COH	-7.20	71.89	14.71	17.83	20.61	23.05	26.99	29.97	0.00	1/ 2/97 THERM	C	2	H	5 O	1 0 G 2
CC.OH	-14.30	67.88	15.81	18.89	21.50	23.78	27.48	30.32	0.00	1/ 2/97 THERM	C	2	H	5 O	1 0 G 2
COC.	1.00	67.28	16.30	19.30	21.70	23.93	27.96	30.87	0.00	1/ 2/97 THERM	C	2	H	5 O	1 0 G 2
CCQ.	-5.49	74.94	18.66	21.81	24.63	27.47	31.44	35.01	0.00	1/ 2/97 THERM	C	2	H	5 O	2 0 G 2
C.CQ	7.41	79.63	20.05	23.37	26.32	29.21	33.02	36.26	0.00	1/ 2/97 THERM	C	2	H	5 O	2 0 G 3
CC.Q	2.31	78.54	20.85	23.81	26.52	29.26	32.98	36.19	0.00	1/ 2/97 THERM	C	2	H	5 O	2 0 G 3
COCO.	-34.47	73.94	18.41	21.69	24.56	27.28	32.14	35.52	0.00	1/ 2/97 THERM	C	2	H	5 O	2 0 G 2
C.OCOH	-42.03	77.54	19.91	22.91	25.37	27.72	32.02	35.05	0.00	1/ 2/97 THERM	C	2	H	5 O	2 0 G 3
COC.OH	-44.53	76.18	19.72	22.69	25.15	27.50	31.85	34.93	0.00	1/ 2/97 THERM	C	2	H	5 O	2 0 G 3
C2H6	-20.40	55.08	12.38	15.68	18.80	21.58	26.04	29.54	35.16	10/31/96	C	2	H	6	0 0 G 1
CCOH	-56.20	67.10	15.48	19.19	22.52	25.45	30.15	33.71	0.00	1/ 2/97 THERM	C	2	H	6 O	1 0 G 2
COC	-43.40	63.76	15.78	19.38	22.50	25.38	30.46	34.14	0.00	1/ 2/97 THERM	C	2	H	6 O	1 0 G 2
CCQ	-41.59	74.72	20.71	24.65	28.18	31.56	36.16	39.98	0.00	1/ 2/97 THERM	C	2	H	6 O	2 0 G 3
COCOH	-86.43	75.40	19.39	22.99	26.17	29.17	34.52	38.32	0.00	1/ 2/97 THERM	C	2	H	6 O	2 0 G 3
C*C*C.	81.62	61.13	13.65	16.07	18.08	19.85	22.46	24.44	27.50	10/31/96	C	3	H	3	0 0 G 0
C#CC.	81.58	59.57	13.76	16.14	18.14	19.80	22.39	24.34	27.47	1/ 2/97 THERM	C	3	H	3	0 0 G 1
C.#CC	124.88	61.39	14.09	15.75	17.43	18.97	21.62	23.68	28.00	1/ 2/97 THERM	C	3	H	3	0 0 G 1
C*C*C	46.72	58.47	14.10	17.12	19.72	22.00	25.44	28.04	32.08	10/31/96	C	3	H	4	0 0 G 0
C#CC	44.28	59.28	14.60	17.31	19.70	21.75	25.09	27.65	32.78	1/ 2/97 THERM	C	3	H	4	0 0 G 1
CC*C*O	-28.20	59.82	13.79	16.13	18.62	20.09	22.45	24.48	27.42	1/17/97 THERM	C	3	H	4 O	1 0 G 1
C*CC*O	-20.32	67.39	17.01	20.92	24.08	26.62	30.56	33.28	0.00	1/17/97 THERM	C	3	H	4 O	1 0 G 1
CC*OC*O	-64.48	76.23	19.10	22.93	26.39	29.37	34.16	37.44	0.00	10/31/96	C	3	H	4 O	2 0 G 2
CC.*C	61.55	65.62	15.11	18.02	20.78	23.27	27.40	30.58	35.63	10/31/96	C	3	H	5	0 0 G 1
C*CC.	40.75	62.05	14.83	18.67	21.94	24.67	28.90	32.03	36.90	10/31/96	C	3	H	5	0 0 G 1
CC*C.	63.75	65.20	15.26	18.48	21.36	23.87	27.92	31.00	35.86	1/2/97	C	3	H	5	0 0 G 1
C*CO.C	-2.91	71.48	17.84	21.27	24.29	27.03	31.82	35.39	40.58	10/31/96	C	3	H	5 O	1 0 G 1
C*COHC.	-2.71	72.21	18.56	22.70	25.99	28.70	33.11	36.26	40.88	10/31/96	C	3	H	5 O	1 0 G 2
C.*COHC	20.29	73.98	18.99	22.51	25.41	27.90	32.13	35.23	39.84	10/31/96	C	3	H	5 O	1 0 G 2
C2.C*O	-9.26	72.49	18.29	22.19	25.74	28.77	33.50	36.93	0.00	10/31/96	C	3	H	5 O	1 0 G 2
CCYC.OC	22.32	70.04	17.26	21.46	25.41	28.31	33.06	36.45	0.00	10/31/96	C	3	H	5 O	1 0 G 1
CCYCOC.	29.52	68.66	17.75	22.25	26.30	29.19	33.79	37.03	0.00	10/31/96	C	3	H	5 O	1 0 G 1

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS			
C*CCO.		22.15	72.99	17.70	21.45	24.85	27.83	32.58	36.01	41.06	10/31/96	C	3	H	5	O	1 0 G 1
C*C.COH		27.09	76.26	18.34	21.54	24.52	27.20	31.62	34.90	39.89	10/31/96	C	3	H	5	O	1 0 G 2
C.*CCOH		29.29	75.84	18.49	22.00	25.10	27.80	32.14	35.32	40.12	10/31/96	C	3	H	5	O	1 0 G 2
C*CC.OH		3.69	70.64	17.14	20.93	24.38	27.40	32.21	35.67	40.80	10/31/96	C	3	H	5	O	1 0 G 2
CCC.*O		-7.60	73.85	18.59	21.98	24.96	27.55	32.16	35.44	0.00	10/31/96	C	3	H	5	O	1 0 G 2
CC.C*O		-4.70	70.36	18.06	21.84	25.19	28.08	32.66	36.06	0.00	10/31/96	C	3	H	5	O	1 0 G 2
C.CC*O		4.50	76.14	18.65	22.05	25.01	27.57	32.16	35.43	0.00	10/31/96	C	3	H	5	O	1 0 G 2
CC*CO.		-1.58	70.39	18.06	21.84	25.19	28.08	32.66	36.06	41.31	12/30/96	C	3	H	5	O	1 0 G 1
C*CCQ.		20.17	82.76	22.05	25.90	29.09	32.15	36.37	40.14	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 2
C*CC.Q		17.57	78.73	22.56	26.92	30.56	33.92	38.34	41.97	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
C*C.CQ		40.97	84.35	23.76	27.53	30.70	33.72	37.75	41.20	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
C.*CCQ		43.17	83.93	23.91	27.99	31.28	34.32	38.27	41.62	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
YC.COOC		14.71	72.96	19.37	25.33	30.80	34.92	40.19	44.53	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 0
YCC.OOC		16.81	71.58	19.37	25.33	30.80	34.92	40.19	44.53	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 0
O*CCCO.		-28.34	81.91	21.54	25.62	29.03	31.95	37.05	40.54	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 2
O*CCC.OH		-38.40	84.15	22.85	26.62	29.62	32.17	36.76	39.95	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
O*CC.COH		-40.50	81.00	21.16	25.35	28.91	31.95	36.77	40.23	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
O*C.CCOH		-43.40	84.49	21.69	25.49	28.68	31.42	36.27	39.61	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
CO.CYCOC		-5.72	76.13	19.70	24.93	29.56	32.92	38.23	41.81	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 1
C.OHCYCOC		-15.78	78.37	21.01	25.93	30.15	33.14	37.94	41.22	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 2
COHCYC.OC		-13.48	80.68	20.36	24.97	29.13	32.18	37.17	40.62	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 2
COHCYCOC.		-11.28	79.30	20.85	25.76	30.02	33.06	37.90	41.20	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 2
CC*OCO.		-33.92	80.45	21.30	25.06	28.40	31.39	36.65	40.39	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 2
CC*OC.OH		-46.98	75.72	20.29	24.91	28.92	32.27	37.37	41.18	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
C.C*OCOH		-43.58	82.93	22.60	26.55	29.86	32.71	37.60	40.97	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
CCO.C*O		-31.24	79.64	21.01	25.73	29.88	32.98	38.10	41.58	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 2
CC.OHC*O		-44.30	74.91	20.00	25.58	30.40	33.86	38.82	42.37	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
C.COHC*O		-34.20	86.31	21.40	25.71	29.44	32.22	36.98	40.32	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
CCOHC.*O		-46.30	82.22	21.16	25.60	29.53	32.45	37.32	40.65	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 3
C.CYCOOC		36.41	75.69	19.28	24.95	30.23	34.00	39.63	44.00	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 1
CCYC.OOC		31.61	73.99	19.73	25.05	30.10	33.77	39.35	43.75	0.00	1/18/97 THERM	C	3	H	5	O	2 0 G 1

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS		
CCYCOOC.	31.31	72.62	19.99	25.79	31.03	34.66	39.94	44.05	0.00	1/18/97 THERM	C	3	H	5 O	2 0 G 1
CC*OCQ.	-34.21	90.80	25.04	29.05	32.41	35.46	40.76	45.02	0.00	10/31/96	C	3	H	5 O	3 0 G 3
C.C*OCQ	-28.01	91.60	27.41	32.08	35.81	38.98	44.05	47.77	0.00	10/31/96	C	3	H	5 O	3 0 G 4
CC*OC.Q	-31.41	94.40	27.23	31.05	34.30	37.25	42.30	46.20	0.00	10/31/96	C	3	H	5 O	3 0 G 4
CC*C	4.65	63.81	15.45	19.23	22.72	25.79	30.74	34.49	40.39	10/31/96	C	3	H	6	0 0 G 1
C*COHC	-38.81	72.59	19.18	23.26	26.77	29.82	34.95	38.72	44.37	10/31/96	C	3	H	6 O	1 0 G 2
C2C*O	-51.56	70.09	17.97	22.00	25.89	29.34	34.93	39.15	0.00	10/31/96	C	3	H	6 O	1 0 G 2
CCC*O	-44.50	72.73	19.42	23.41	26.92	29.97	35.32	39.17	0.00	10/31/96	C	3	H	6 O	1 0 G 2
CCYCOC	-21.88	66.95	17.58	22.72	27.45	30.94	36.50	40.44	0.00	10/31/96	C	3	H	6 O	1 0 G 1
C*CCOH	-29.81	74.45	18.68	22.75	26.46	29.72	34.96	38.81	44.65	10/31/96	C	3	H	6 O	1 0 G 2
C*COC	-25.54	71.74	19.95	24.97	29.15	32.48	37.52	41.40	0.00	12/22/96 THERM	C	3	H	6 O	1 0 G 2
CC*COH	-37.48	71.50	19.40	23.83	27.67	30.87	35.79	39.39	45.10	12/24/96 THERM	C	3	H	6 O	1 0 G 2
C*CQC	-15.57	82.84	23.59	28.35	32.07	35.40	40.81	44.61	0.00	10/31/96	C	3	H	6 O	2 0 G 3
CC*CQ	-15.47	79.71	23.65	28.52	32.79	36.37	41.84	45.69	0.00	12/25/96 THERM	C	3	H	6 O	2 0 G 3
C*CCQ	-15.93	82.54	24.10	28.74	32.64	36.24	41.09	45.11	0.00	1/18/97 THERM	C	3	H	6 O	2 0 G 3
YCCOOC	-29.19	69.86	19.43	25.85	31.91	36.66	43.04	48.22	0.00	1/18/97 THERM	C	3	H	6 O	2 0 G 0
O*CCCOH	-80.30	83.37	22.52	26.92	30.64	33.84	39.43	43.34	0.00	1/18/97 THERM	C	3	H	6 O	2 0 G 3
COHCYCOC	-57.68	77.59	20.68	26.23	31.17	34.81	40.61	44.61	0.00	1/18/97 THERM	C	3	H	6 O	2 0 G 2
CCOHCHO	-83.20	82.47	21.99	27.03	31.49	34.87	40.48	44.38	0.00	2/ 9/97 THERM	C	3	H	6 O	2 0 G 3
CCYCOOC	-12.59	70.90	20.05	26.31	32.14	36.40	42.79	47.74	0.00	2/ 9/97 THERM	C	3	H	6 O	2 0 G 1
OHCYCCOC	-58.53	73.19	18.75	24.90	30.36	34.39	40.66	44.91	0.00	2/ 9/97 THERM	C	3	H	6 O	2 0 G 1
YCOCICOH	-66.71	73.46	21.41	26.77	31.42	35.14	40.91	44.89	0.00	2/ 9/97 THERM	C	3	H	6 O	2 0 G 2
CC*OCOH	-85.88	81.91	22.28	26.36	30.01	33.28	39.03	43.19	0.00	2/ 9/97 THERM	C	3	H	6 O	2 0 G 3
CQCYCOC	-43.07	85.21	25.91	31.69	36.83	40.92	46.62	50.88	0.00	2/ 9/97 THERM	C	3	H	6 O	3 0 G 3
QCYCCOC	-43.01	80.00	23.60	30.08	35.59	40.27	46.40	50.91	0.00	2/ 9/97 THERM	C	3	H	6 O	3 0 G 2
CC*OCQ	-71.31	90.93	27.09	31.89	35.96	39.55	45.48	49.99	0.00	2/ 9/97 THERM	C	3	H	6 O	3 0 G 4
YCOCICQ	-51.54	81.03	26.22	32.30	37.37	41.41	47.36	51.69	0.00	2/ 9/97 THERM	C	3	H	6 O	3 0 G 3
CCQCHO	-67.63	90.74	26.80	32.56	37.44	41.14	46.93	51.18	0.00	2/ 9/97 THERM	C	3	H	6 O	3 0 G 4
CCC.	23.67	70.67	17.11	21.27	25.14	28.53	33.95	38.14	44.70	10/31/96	C	3	H	7	0 0 G 2
CC.C	21.02	68.94	16.38	20.30	23.95	27.54	33.36	37.43	44.16	10/31/96	C	3	H	7	0 0 G 2
C2CO.	-13.54	73.06	20.50	25.52	30.11	33.65	39.49	43.75	50.52	12/30/96 THERM	C	3	H	7 O	1 0 G 2

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS		
C2C.OH	-24.80	78.99	20.71	24.89	28.90	32.13	37.75	42.02	48.99	12/30/96 THERM	C	3	H	7 O	1 0 G 3
CCCO.	-9.17	75.06	20.00	24.84	29.16	32.91	38.84	43.25	0.00	2/ 9/97 THERM	C	3	H	7 O	1 0 G 2
CCC.OH	-19.23	77.30	21.31	25.84	29.75	33.13	38.55	42.66	0.00	2/ 9/97 THERM	C	3	H	7 O	1 0 G 3
CC.COH	-14.78	81.65	19.44	23.37	27.28	30.90	36.87	41.41	0.00	2/ 9/97 THERM	C	3	H	7 O	1 0 G 3
C.CCOH	-12.13	81.31	20.21	24.78	28.86	32.40	38.06	42.31	0.00	2/ 9/97 THERM	C	3	H	7 O	1 0 G 3
C2.COH	-16.50	79.74	20.89	25.50	29.67	32.89	38.37	42.49	49.24	2/ 9/97 THERM	C	3	H	7 O	1 0 G 3
C2C.Q	-8.48	87.31	26.55	30.69	34.50	38.21	43.48	47.93	0.00	10/31/96	C	3	H	7 O	2 0 G 4
C2CQ.	-13.88	81.55	24.28	29.16	33.40	37.33	42.89	47.58	0.00	10/31/96	C	3	H	7 O	2 0 G 3
C.CCQ	2.48	88.93	25.44	30.24	34.52	38.51	44.07	48.58	0.00	10/31/96	C	3	H	7 O	2 0 G 4
CCCQ.	-10.42	84.36	24.16	28.76	32.88	36.82	42.51	47.35	0.00	2/9/97	C	3	H	7 O	2 0 G 3
CC.CQ	-0.17	87.21	25.60	30.05	34.15	38.10	43.69	48.27	0.00	2/9/97	C	3	H	7 O	2 0 G 4
CCC.Q	-2.62	87.96	26.35	30.76	34.77	38.61	44.05	48.53	0.00	2/9/97	C	3	H	7 O	2 0 G 4
CCOHCQ.	-50.59	94.38	27.76	32.95	37.55	41.43	47.27	52.02	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 4
CCO.CQ	-34.73	92.70	28.83	34.49	39.49	43.63	49.61	54.19	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 4
CCOHC.Q	-42.79	97.98	29.95	34.95	39.44	43.22	48.81	53.20	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 5
CC.OHCQ	-45.99	98.63	29.04	33.86	38.28	42.11	47.87	52.46	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 5
C.COHCQ	-37.69	99.37	29.22	34.47	39.05	42.87	48.49	52.93	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 5
CCQ.COH	-49.68	93.57	27.38	32.67	37.12	41.20	47.00	51.75	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 4
CCQCO.	-33.82	91.89	28.45	34.21	39.06	43.40	49.34	53.92	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 4
CCQC.OH	-43.88	94.13	29.76	35.21	39.65	43.62	49.05	53.33	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 5
CC.QCOH	-44.28	99.33	29.65	34.20	38.22	42.08	47.59	52.10	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 5
C.CQCOH	-36.78	98.29	28.78	34.23	38.79	42.91	48.56	52.97	0.00	2/ 9/97 THERM	C	3	H	7 O	3 0 G 5
CCQCQ.	-35.07	101.19	32.61	38.13	42.78	47.31	53.01	58.02	0.00	2/ 9/97 THERM	C	3	H	7 O	4 0 G 5
CCQ.CQ	-35.07	101.19	32.61	38.13	42.78	47.31	53.01	58.02	0.00	2/ 9/97 THERM	C	3	H	7 O	4 0 G 5
C.CQCQ	-22.17	105.91	34.01	39.69	44.45	49.02	54.57	59.24	0.00	2/ 9/97 THERM	C	3	H	7 O	4 0 G 6
CC.QCQ	-29.67	106.95	34.88	39.66	43.88	48.19	53.60	58.37	0.00	2/ 9/97 THERM	C	3	H	7 O	4 0 G 6
CCQC.Q	-27.27	104.79	34.80	40.13	44.67	49.10	54.55	59.20	0.00	2/ 9/97 THERM	C	3	H	7 O	4 0 G 6
CCC	-25.33	64.50	17.88	22.63	27.05	30.93	37.11	41.88	49.36	10/31/96	C	3	H	8	0 0 G 2
CCCOH	-61.13	76.52	20.98	26.14	30.77	34.80	41.22	46.05	0.00	2/ 9/97 THERM	C	3	H	8 O	1 0 G 3
C2COH	-65.50	74.52	21.48	26.82	31.72	35.54	41.87	46.55	54.11	2/ 9/97 THERM	C	3	H	8 O	1 0 G 3
C2CQ	-49.98	81.33	26.33	32.00	36.95	41.42	47.61	52.55	0.00	10/31/96	C	3	H	8 O	2 0 G 4

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS			
CCCQ	-46.52	84.14	26.21	31.60	36.43	40.91	47.23	52.32	0.00	10/31/96	C	3	H	8	O	2 0 G 4
CCOHCQ	-86.69	94.16	29.81	35.79	41.10	45.52	51.99	56.99	0.00	2/ 9/97 THERM	C	3	H	8	O	3 0 G 5
CCQCOH	-85.78	93.35	29.43	35.51	40.67	45.29	51.72	56.72	0.00	2/ 9/97 THERM	C	3	H	8	O	3 0 G 5
CCQCQ	-71.17	100.97	34.66	40.97	46.33	51.40	57.73	62.99	0.00	2/ 9/97 THERM	C	3	H	8	O	4 0 G 6
C*CICC.*O	3.56	73.25	22.95	27.49	31.07	33.96	38.52	41.67	0.00	10/31/96	C	4	H	5	O	1 0 G 2
C2C*C*O	-28.06	73.97	24.08	28.58	33.01	36.14	41.27	45.33	51.36	10/31/96	C	4	H	6	O	1 0 G 2
C*CICC*O	-27.34	74.64	23.14	28.34	32.66	36.17	41.73	45.56	0.00	10/31/96	C	4	H	6	O	1 0 G 2
C*CYCCOC	5.85	67.28	19.11	24.75	29.98	34.31	40.92	45.55	0.00	10/31/96	C	4	H	6	O	1 0 G 0
C2.C*C	32.30	70.99	20.96	26.09	30.52	34.22	40.07	44.43	51.22	10/31/96	C	4	H	7		0 0 G 2
C2C*C.	55.30	72.75	21.39	25.90	29.94	33.42	39.09	43.40	50.18	10/31/96	C	4	H	7		0 0 G 2
C2.CC*O	-2.20	84.87	22.98	28.14	32.91	36.80	43.20	47.87	0.00	10/31/96	C	4	H	7	O	1 0 G 3
C2C.C*O	-13.50	77.94	24.19	29.26	33.73	37.63	43.83	48.46	0.00	10/31/96	C	4	H	7	O	1 0 G 3
C2CC.*O	-14.30	80.77	22.74	28.03	33.00	37.03	43.54	48.20	0.00	10/31/96	C	4	H	7	O	1 0 G 3
C2CC*O.	7.90	81.04	23.38	28.71	33.60	37.53	43.88	48.44	0.00	10/31/96	C	4	H	7	O	1 0 G 3
C2CYCOC.	19.92	74.32	23.47	29.64	34.85	38.95	45.20	49.64	0.00	10/31/96	C	4	H	7	O	1 0 G 2
C*CIC.COH	-2.16	81.63	24.19	29.61	34.26	38.15	44.29	48.75	55.48	10/31/96	C	4	H	7	O	1 0 G 3
C*CICC.OH	-4.76	78.20	23.27	28.35	32.96	36.95	43.38	48.07	55.12	10/31/96	C	4	H	7	O	1 0 G 3
C.*CICCOH	20.84	83.40	24.62	29.42	33.68	37.35	43.31	47.72	54.44	10/31/96	C	4	H	7	O	1 0 G 3
C*CICCO.	13.70	80.55	23.83	28.87	33.43	37.38	43.75	48.41	55.38	10/31/96	C	4	H	7	O	1 0 G 2
C2C*CO.	-10.03	77.94	24.19	29.26	33.77	37.63	43.83	48.46	55.63	12/30/96	C	4	H	7	O	1 0 G 2
C*CICCQ.	11.72	90.32	28.18	33.32	37.67	41.70	47.54	52.54	0.00	10/31/96	C	4	H	7	O	2 0 G 3
C2CO.C*O	-39.04	84.24	26.72	32.79	38.26	42.86	49.80	54.51	0.00	10/31/96	C	4	H	7	O	2 0 G 3
C2.COHC*O	-42.00	90.92	27.11	32.77	37.82	42.10	48.68	53.25	0.00	10/31/96	C	4	H	7	O	2 0 G 4
C*CICC.Q	9.12	86.29	28.69	34.34	39.14	43.47	49.51	54.37	0.00	10/31/96	C	4	H	7	O	2 0 G 4
C*CIC.CQ	11.72	89.72	29.61	35.60	40.44	44.67	50.42	55.05	0.00	10/31/96	C	4	H	7	O	2 0 G 4
C.*CICCQ	34.72	91.49	30.04	35.41	39.86	43.87	49.44	54.02	0.00	10/31/96	C	4	H	7	O	2 0 G 4
C2.CYCOOC	27.81	81.41	25.00	32.34	38.78	43.76	51.04	56.61	0.00	10/31/96	C	4	H	7	O	2 0 G 2
C2CYCOOC	22.71	78.33	25.71	33.18	39.58	44.42	51.35	56.66	0.00	10/31/96	C	4	H	7	O	2 0 G 2
CCYC.COC	18.67	74.37	20.06	26.34	31.97	36.64	43.72	48.73	0.00	10/31/96	C	4	H	7	O	2 0 G 1
CCYCC.OC	18.37	73.00	20.32	27.08	32.90	37.53	44.31	49.03	0.00	10/31/96	C	4	H	7	O	2 0 G 1
CCYC.COOC	9.84	80.37	24.34	31.48	38.19	43.52	50.86	56.71	0.00	10/31/96	C	4	H	7	O	2 0 G 1

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS		
CCYCC.OOC	9.54	79.00	24.60	32.22	39.12	44.41	51.45	57.01	0.00	10/31/96	C	4	H	7 O	2 0 G 1
CCICO.C*O	-35.04	90.21	25.69	31.67	37.07	41.43	48.43	53.30	0.00	10/31/96	C	4	H	7 O	2 0 G 3
YCOCICCO.	-15.32	81.80	25.42	32.32	38.11	42.68	49.64	54.42	0.00	10/31/96	C	4	H	7 O	2 0 G 2
C2CQC.*O	-38.53	95.49	31.68	38.19	43.86	48.60	55.47	60.38	0.00	10/31/96	C	4	H	7 O	3 0 G 5
C2.CQC*O	-26.43	99.59	31.92	38.30	43.77	48.37	55.13	60.05	0.00	10/31/96	C	4	H	7 O	3 0 G 5
C2CQ.C*O	-39.33	94.59	30.46	36.78	42.27	46.93	53.91	59.14	0.00	10/31/96	C	4	H	7 O	3 0 G 4
C2C.OOC*O	-44.03	102.48	29.65	35.70	41.10	45.24	52.76	58.29	0.00	10/31/96	C	4	H	7 O	3 0 G 5
C2YC2O2O.	-15.03	82.35	29.35	37.15	44.41	49.62	57.04	62.88	0.00	10/31/96	C	4	H	7 O	3 0 G 2
C2C*C	-3.80	69.99	21.58	26.65	31.30	35.34	41.91	46.89	54.71	10/31/96	C	4	H	8	0 0 G 2
C2CC*O	-51.20	79.65	23.57	29.46	34.96	39.45	46.70	51.93	0.00	10/31/96	C	4	H	8 O	1 0 G 3
CC*OCC	-56.88	81.06	24.17	29.70	34.59	38.84	46.03	51.35	0.00	10/31/96	C	4	H	8 O	1 0 G 3
C2CYCOC	-31.48	72.61	23.30	30.11	36.00	40.70	47.91	53.05	0.00	10/31/96	C	4	H	8 O	1 0 G 2
CCYCCOC	-25.53	71.28	20.38	27.60	34.01	39.27	47.16	52.72	0.00	10/31/96	C	4	H	8 O	1 0 G 1
C*CICCOH	-38.26	82.01	24.81	30.17	35.04	39.27	46.13	51.21	58.97	10/31/96	C	4	H	8 O	1 0 G 3
C2C*COH	-45.93	79.05	25.53	31.25	36.25	40.42	46.96	51.79	59.42	10/31/96	C	4	H	8 O	1 0 G 3
C*CICOC	-34.74	81.44	24.98	30.91	35.95	40.22	47.28	52.68	0.00	12/22/96 THERM	C	4	H	8 O	1 0 G 3
C2COHC*O	-91.00	85.70	27.70	34.09	39.87	44.75	52.18	57.31	0.00	10/31/96	C	4	H	8 O	2 0 G 4
C*CICCQ	-24.38	90.10	30.23	36.16	41.22	45.79	52.26	57.51	0.00	10/31/96	C	4	H	8 O	2 0 G 4
C2C*CQ	-23.92	87.26	29.78	35.94	41.37	45.92	53.01	58.09	0.00	10/31/96	C	4	H	8 O	2 0 G 4
C2CYCOOC	-21.19	76.61	25.77	33.70	40.69	46.16	54.20	60.35	0.00	10/31/96	C	4	H	8 O	2 0 G 2
CCYCCOOC	-34.36	77.28	24.66	32.74	40.23	46.15	54.30	60.70	0.00	10/31/96	C	4	H	8 O	2 0 G 1
CCICOHC*O	-87.00	91.67	26.67	32.97	38.68	43.32	50.81	56.10	0.00	10/31/96	C	4	H	8 O	2 0 G 4
YCOCICCOH	-67.28	83.26	26.40	33.62	39.72	44.57	52.02	57.22	0.00	10/31/96	C	4	H	8 O	2 0 G 3
CCYC3O(Q)	-52.71	85.08	29.60	37.67	44.44	50.11	57.72	63.32	0.00	10/31/96	C	4	H	8 O	3 0 G 3
C2CQC*O	-75.43	94.37	32.51	39.62	45.82	51.02	58.63	64.11	0.00	10/31/96	C	4	H	8 O	3 0 G 5
C2COOC*O	-84.73	100.02	31.14	38.58	45.00	49.75	57.85	63.61	0.00	10/31/96	C	4	H	8 O	3 0 G 5
C2YC2O2OH	-66.99	83.81	30.33	38.45	46.02	51.51	59.42	65.68	0.00	10/31/96	C	4	H	8 O	3 0 G 3
C*CICOHCQ	-58.84	100.74	33.46	39.68	44.96	49.72	56.48	61.83	0.00	10/31/96	C	4	H	8 O	3 0 G 5
C2CYC2O3	-13.43	85.87	27.85	37.56	45.61	51.50	59.72	66.23	0.00	10/31/96	C	4	H	8 O	3 0 G 2
YCOCICCQ	-52.67	90.88	31.63	39.08	45.38	50.68	58.03	63.49	0.00	10/31/96	C	4	H	8 O	3 0 G 4
C2CYC2O3	-26.46	83.61	27.85	37.56	45.61	51.50	59.72	66.23	0.00	10/31/96	C	4	H	8 O	3 0 G 2

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS		
C3.C	16.50	77.82	22.52	28.20	33.32	37.77	44.87	50.30	59.05	10/31/96	C	4	H	9	0 0 G 3
C3C.	11.90	75.67	22.33	27.04	31.82	36.27	43.62	49.34	58.53	10/31/96	C	4	H	9	0 0 G 3
C3.COH	-26.10	85.40	26.61	32.89	38.22	42.65	49.78	55.10	0.00	10/31/96	C	4	H	9 O	1 0 G 4
C3CO.	-23.14	76.55	26.22	32.91	38.66	43.41	50.90	56.36	0.00	10/31/96	C	4	H	9 O	1 0 G 3
C2C.COH	-23.90	87.12	25.43	30.55	35.54	40.14	47.73	53.51	0.00	10/31/96	C	4	H	9 O	1 0 G 4
C2CCO.	-16.34	80.42	25.23	31.73	37.48	42.40	50.10	55.73	0.00	10/31/96	C	4	H	9 O	1 0 G 3
C2.CCOH	-19.30	88.05	25.44	31.67	37.18	41.89	49.32	54.79	0.00	10/31/96	C	4	H	9 O	1 0 G 4
C2CC.OH	-26.40	84.03	26.54	32.73	38.07	42.62	49.81	55.14	0.00	10/31/96	C	4	H	9 O	1 0 G 4
C3.COH	-26.10	85.40	26.61	32.89	38.22	42.65	49.78	55.10	0.00	10/31/96	C	4	H	9 O	1 0 G 4
C2C.OC	-19.40	84.82	25.28	30.98	36.10	40.39	48.19	53.99	0.00	10/31/96	C	4	H	9 O	1 0 G 4
C2COC.	-15.70	85.88	27.29	33.78	39.20	43.45	50.78	56.04	0.00	10/31/96	C	4	H	9 O	1 0 G 4
C2.COC	-11.10	87.57	26.18	32.54	37.95	42.25	49.78	55.25	0.00	10/31/96	C	4	H	9 O	1 0 G 4
C3.CQ	-10.68	91.62	31.74	38.27	43.75	48.61	55.43	60.90	0.00	10/31/96	C	4	H	9 O	2 0 G 5
C3CQ.	-23.58	84.45	30.28	36.75	42.25	47.17	54.21	59.99	0.00	10/31/96	C	4	H	9 O	2 0 G 4
C2C.CQ	-9.29	96.11	30.66	36.01	41.20	46.25	53.74	59.78	0.00	10/31/96	C	4	H	9 O	2 0 G 5
C2CCQ.	-17.59	91.09	29.39	35.65	41.20	46.31	53.77	59.83	0.00	10/31/96	C	4	H	9 O	2 0 G 4
C2CC.Q	-9.79	94.69	31.58	37.65	43.09	48.10	55.31	61.01	0.00	10/31/96	C	4	H	9 O	2 0 G 5
C2.CCQ	-4.69	96.09	30.85	37.17	42.70	47.75	54.99	60.74	0.00	10/31/96	C	4	H	9 O	2 0 G 5
C2COHCQ.	-60.19	98.67	33.48	40.34	46.10	51.19	58.68	64.63	0.00	10/31/96	C	4	H	9 O	3 0 G 5
C2CO.CQ	-44.33	96.99	34.55	41.88	48.04	53.39	61.02	66.80	0.00	10/31/96	C	4	H	9 O	3 0 G 5
C2.COHCQ	-47.29	103.67	34.94	41.86	47.60	52.63	59.90	65.54	0.00	10/31/96	C	4	H	9 O	3 0 G 6
C2COHC.Q	-52.39	102.27	35.67	42.34	47.99	52.98	60.22	65.81	0.00	10/31/96	C	4	H	9 O	3 0 G 6
C2CQ.COH	-59.38	97.27	33.38	40.26	45.97	51.04	58.32	64.16	0.00	10/31/96	C	4	H	9 O	3 0 G 5
C2CQCO.	-43.52	95.59	34.45	41.80	47.91	53.24	60.66	66.33	0.00	10/31/96	C	4	H	9 O	3 0 G 5
C2.CQCOH	-46.48	102.27	34.84	41.78	47.47	52.48	59.54	65.07	0.00	10/31/96	C	4	H	9 O	3 0 G 6
C2CQC.OH	-53.58	97.83	35.76	42.80	48.50	53.46	60.37	65.74	0.00	10/31/96	C	4	H	9 O	3 0 G 6
C2CQ.CQ	-47.67	104.90	38.78	45.97	51.89	57.36	64.38	70.37	0.00	12/27/96 modif	C	4	H	9 O	4 0 G 6
C2CQCQ.	-44.77	104.89	38.61	45.72	51.63	57.15	64.33	70.43	0.00	10/31/96	C	4	H	9 O	4 0 G 6
C2.CQCQ	-31.87	109.89	40.07	47.24	53.13	58.59	65.55	71.34	0.00	10/31/96	C	4	H	9 O	4 0 G 7
C2CQC.Q	-36.97	108.49	40.80	47.72	53.52	58.94	65.87	71.61	0.00	10/31/96	C	4	H	9 O	4 0 G 7
C3C	-32.50	70.43	23.11	29.52	35.37	40.42	48.37	54.36	63.92	10/31/96	C	4	H	10	0 0 G 3

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS			
C3COH	-75.10	78.01	27.20	34.21	40.27	45.30	53.28	59.16	0.00	10/31/96	C	4	H	10	O	1 0 G 4
C2CCOH	-68.30	83.25	26.21	33.03	39.09	44.29	52.48	58.53	0.00	10/31/96	C	4	H	10	O	1 0 G 4
C2COC	-60.10	82.36	26.77	33.86	40.00	44.90	53.28	59.31	0.00	10/31/96	C	4	H	10	O	1 0 G 4
C3CQ	-59.68	84.23	32.33	39.59	45.80	51.26	58.93	64.96	0.00	10/31/96	C	4	H	10	O	2 0 G 5
C2CCQ	-53.69	90.87	31.44	38.49	44.75	50.40	58.49	64.80	0.00	10/31/96	C	4	H	10	O	2 0 G 5
C2COHCQ	-96.29	98.45	35.53	43.18	49.65	55.28	63.40	69.60	0.00	10/31/96	C	4	H	10	O	3 0 G 6
C2CQCOH	-95.48	97.05	35.43	43.10	49.52	55.13	63.04	69.13	0.00	10/31/96	C	4	H	10	O	3 0 G 6
C2CQCQ	-80.87	104.67	40.66	48.56	55.18	61.24	69.05	75.40	0.00	10/31/96	C	4	H	10	O	4 0 G 7
C2CYCC.OC	10.57	78.19	26.34	35.05	42.49	48.39	56.79	62.51	0.00	10/31/96	C	5	H	9	O	1 0 G 2
C2.CYCCOC	15.67	81.27	25.63	34.21	41.69	47.73	56.48	62.46	0.00	10/31/96	C	5	H	9	O	1 0 G 2
C3.CC*O	-9.30	90.07	29.00	36.11	42.40	47.66	55.68	61.41	0.00	10/31/96	C	5	H	9	O	1 0 G 4
C3CC.*O	-21.40	83.80	28.76	36.00	42.49	47.89	56.02	61.74	0.00	10/31/96	C	5	H	9	O	1 0 G 4
C2ClCO.CO	-42.14	94.04	31.71	39.64	46.56	52.29	60.91	66.84	0.00	10/31/96	C	5	H	9	O	2 0 G 4
C5TOH.*O	-57.20	96.62	31.86	39.51	46.21	51.76	60.13	65.91	0.00	10/31/96	C	5	H	9	O	2 0 G 5
C5.TOH*O	-45.10	100.72	32.10	39.62	46.12	51.53	59.79	65.58	0.00	10/31/96	C	5	H	9	O	2 0 G 5
C5TO.*O	-42.14	94.04	31.71	39.64	46.56	52.29	60.91	66.84	0.00	10/31/96	C	5	H	9	O	2 0 G 5
C3CC.I	26.90	93.44	31.39	39.51	46.29	51.93	60.55	66.59	75.51	1/30/95 THERM	C	5	H	10	I	1 0 G 4
C3.CCI	26.90	97.79	31.55	39.33	46.41	51.74	60.13	66.21	0.00	10/31/96	C	5	H	10	I	1 0 G 4
C3CC.I	26.90	93.43	31.55	39.33	46.41	51.74	60.13	66.21	0.00	10/31/96	C	5	H	10	I	1 0 G 4
C3CC*O	-58.30	82.68	29.59	37.43	44.45	50.31	59.18	65.47	0.00	10/31/96	C	5	H	10	O	1 0 G 4
C2CYCCOC	-33.33	76.47	26.40	35.57	43.60	50.13	59.64	66.20	0.00	10/31/96	C	5	H	10	O	1 0 G 2
C2ClCQC*O	-79.49	103.12	37.92	46.40	53.83	60.29	69.30	75.91	0.00	10/31/96	C	5	H	10	O	3 0 G 6
C3CC.	8.70	80.84	28.54	36.17	42.91	48.63	57.35	63.78	73.57	10/31/96	C	5	H	11		0 0 G 4
C3CCI	-22.10	90.40	32.14	40.65	48.46	54.39	63.63	70.27	0.00	10/31/96	C	5	H	11	I	1 0 G 4
C3CCO.	-24.14	84.81	31.25	39.70	47.07	53.26	62.58	69.21	0.00	10/31/96	C	5	H	11	O	1 0 G 4
C3.CCOH	-27.10	93.66	31.64	39.68	46.63	52.50	61.46	67.95	0.00	10/31/96	C	5	H	11	O	1 0 G 5
C3CC.OH	-34.20	87.05	32.56	40.70	47.66	53.48	62.29	68.62	0.00	10/31/96	C	5	H	11	O	1 0 G 5
C3.COC	-19.90	93.24	31.90	39.93	46.50	52.01	61.19	67.86	0.00	10/31/96	C	5	H	11	O	1 0 G 5
C3COC.	-24.50	89.37	33.01	41.17	47.75	53.21	62.19	68.65	0.00	10/31/96	C	5	H	11	O	1 0 G 5
C3CCOO.	-25.39	94.11	35.41	43.62	50.79	57.17	66.25	73.31	0.00	10/31/96	C	5	H	11	O	2 0 G 5
C3.CCOOH	-12.49	101.28	36.87	45.14	52.29	58.61	67.47	74.22	0.00	10/31/96	C	5	H	11	O	2 0 G 6

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS				
C3CC.OOH	-17.59	97.71	37.60	45.62	52.68	58.96	67.79	74.49	0.00	10/31/96	C	5	H	11	O	2	0 G 6
C2ClCQCQ.	-46.58	114.55	43.74	52.59	60.17	67.15	76.37	83.75	0.00	10/31/96	C	5	H	11	O	4	0 G 7
C2.ClCQCQ	-33.68	119.55	45.20	54.11	61.67	68.59	77.59	84.66	0.00	10/31/96	C	5	H	11	O	4	0 G 8
C2ClCQCQ.	-38.78	118.15	45.93	54.59	62.06	68.94	77.91	84.93	0.00	10/31/96	C	5	H	11	O	4	0 G 8
C4C	-40.30	72.87	29.13	37.49	44.96	51.28	60.85	67.84	78.44	10/31/96	C	5	H	12		0	0 G 4
C3CCOH	-76.10	86.27	32.23	41.00	48.68	55.15	64.96	72.01	0.00	10/31/96	C	5	H	12	O	1	0 G 5
C3COC	-68.90	85.85	32.49	41.25	48.55	54.66	64.69	71.92	0.00	10/31/96	C	5	H	12	O	1	0 G 5
C3CCOOH	-61.49	93.89	37.46	46.46	54.34	61.26	70.97	78.28	0.00	10/31/96	C	5	H	12	O	2	0 G 6
C2ClCOHCO	-94.10	95.50	32.69	40.94	48.17	54.18	63.29	69.64	0.00	10/31/96	C	5	H	12	O	2	0 G 5
C2ClCQCQ	-82.68	114.33	45.79	55.43	63.72	71.24	81.09	88.72	0.00	10/31/96	C	5	H	12	O	4	0 G 8
C6H6	19.80	64.24	19.44	26.64	32.76	37.80	45.24	50.46	58.38	10/31/96	C	6	H	6		0	0 G 0
DE15	20.18	86.63	28.76	36.50	43.28	48.98	57.88	64.40	74.34	10/31/96	C	6	H	10		0	0 G 3
M2DE15	11.73	98.32	34.89	43.92	51.86	58.53	69.05	76.80	88.66	10/31/96	C	7	H	12		0	0 G 4
DM25DE15	3.28	104.50	41.02	51.34	60.44	68.08	80.22	89.20	102.98	10/31/96	C	8	H	14		0	0 G 5
C3.CCC3	-3.20	102.19	45.29	57.98	69.07	78.33	92.16	102.08	116.85	10/31/96	C	8	H	17		0	0 G 7
C3CCC3	-52.20	93.42	45.88	59.30	71.12	80.98	95.66	106.14	121.72	10/31/96	C	8	H	18		0	0 G 7
CYC3OICOH	-68.13	78.86	24.47	32.29	38.91	44.15	52.07	57.52	0.00	3/ 7/97 THERM	C	4	H	8	O	2	0 G 2
C*ClCOOC	-14.57	92.12	28.31	34.90	40.32	44.96	52.55	57.68	0.00	3/16/97 THERM	C	4	H	8	O	2	0 G 4
C*ClCOOC.	31.83	95.42	28.93	34.99	39.79	43.87	50.54	54.93	0.00	3/16/97 THERM	C	4	H	7	O	2	0 G 4
C*COOC	-5.37	80.23	23.28	28.96	33.52	37.22	42.79	46.40	0.00	3/16/97 THERM	C	3	H	6	O	2	0 G 3
C*COOC.	41.03	83.53	23.90	29.05	32.99	36.13	40.78	43.65	0.00	3/16/97 THERM	C	3	H	5	O	2	0 G 3
COHCQ	-77.39	85.36	23.81	28.16	31.90	35.43	40.27	44.15	0.00	3/20/97 THERM	C	2	H	6	O	3	0 G 4
CO.CQ	-25.43	83.90	22.83	26.86	30.29	33.54	37.89	41.35	0.00	3/20/97 THERM	C	2	H	5	O	3	0 G 3
COHCQ.	-41.29	85.58	21.76	25.32	28.35	31.34	35.55	39.18	0.00	3/20/97 THERM	C	2	H	5	O	3	0 G 3
COHC.Q	-33.49	89.18	23.95	27.32	30.24	33.13	37.09	40.36	0.00	3/20/97 THERM	C	2	H	5	O	3	0 G 4
C.OHCQ	-35.49	86.14	24.14	27.86	30.88	33.76	37.60	40.76	0.00	3/20/97 THERM	C	2	H	5	O	3	0 G 4
QCCHO	-58.93	82.59	22.34	25.60	28.29	30.68	34.77	37.81	0.00	3/20/97 THERM	C	2	H	4	O	3	0 G 3
Q.CCHO	-22.83	82.81	20.29	22.76	24.74	26.59	30.05	32.84	0.00	3/20/97 THERM	C	2	H	3	O	3	0 G 2
QC.CHO	-20.03	76.40	20.35	24.15	27.20	29.67	33.11	35.80	0.00	3/20/97 THERM	C	2	H	3	O	3	0 G 3
QCC.*O	-22.03	83.71	21.51	24.17	26.33	28.26	31.61	34.08	0.00	3/20/97 THERM	C	2	H	3	O	3	0 G 3
COHCOH	-92.00	76.36	18.58	22.70	26.24	29.32	34.26	37.88	0.00	3/20/97 THERM	C	2	H	6	O	2	0 G 3

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500	DATE	ELEME	N	TS		
CO.COH	-40.04	76.28	17.60	21.40	24.63	27.43	31.88	35.08	0.00	3/20/97 THERM	C	2 H	5 O	2 0 G	2
C.OHCOH	-50.10	78.52	18.91	22.40	25.22	27.65	31.59	34.49	0.00	3/20/97 THERM	C	2 H	5 O	2 0 G	3
QCCQ	-62.78	91.60	29.04	33.62	37.56	41.54	46.28	50.42	0.00	3/20/97 THERM	C	2 H	6 O	4 0 G	5
QCCQ.	-26.68	93.20	26.99	30.78	34.01	37.45	41.56	45.45	0.00	3/21/97	C	2 H	5 O	4 0 G	4
QCC.Q	-18.88	96.80	29.18	32.78	35.90	39.24	43.10	46.63	0.00	3/20/97 THERM	C	2 H	5 O	4 0 G	5
COHCHO	-73.50	73.57	17.53	20.07	22.34	24.41	28.32	31.01	0.00	3/20/97 THERM	C	2 H	4 O	2 0 G	2
CO.CHO	-21.54	72.11	16.55	18.77	20.73	22.52	25.94	28.21	0.00	3/20/97 THERM	C	2 H	3 O	2 0 G	1
C.OHCHO	-34.60	67.38	15.54	18.62	21.25	23.40	26.66	29.00	0.00	3/20/97 THERM	C	2 H	3 O	2 0 G	2
COHC.*O	-36.60	74.69	16.70	18.64	20.38	21.99	25.16	27.28	0.00	3/20/97 THERM	C	2 H	3 O	2 0 G	2
COCQ	-71.86	86.60	24.20	28.52	32.12	35.44	40.97	45.12	0.00	3/20/97 THERM	C	2 H	6 O	3 0 G	4
COCQ.	-35.76	86.82	22.15	25.68	28.57	31.35	36.25	40.15	0.00	3/20/97 THERM	C	2 H	5 O	3 0 G	3
COC.Q	-27.96	90.42	24.34	27.68	30.46	33.14	37.79	41.33	0.00	3/20/97 THERM	C	2 H	5 O	3 0 G	4
C.OCQ	-27.46	87.94	24.72	28.44	31.32	33.99	38.47	41.85	0.00	3/20/97 THERM	C	2 H	5 O	3 0 G	4
C2COHC.*O	-54.10	86.82	26.87	32.66	37.91	42.33	49.02	53.58	0.00	3/21/97 THERM	C	4 H	7 O	2 0 G	4
CCQC.*O	-30.73	91.86	25.97	31.13	35.48	38.72	43.77	47.45	0.00	3/21/97 THERM	C	3 H	5 O	3 0 G	4
C2.CQ	-0.98	87.65	25.68	30.72	35.07	39.04	44.45	48.80	0.00	4/2/97	C	3 H	7 O	2 0 G	4
C2C*CB	-3.80	69.99	21.58	26.65	31.30	35.34	41.91	46.89	54.71	10/31/96	C	4 H	8	0 0 G	2
HO2B	3.50	54.73	8.37	8.95	9.48	9.96	10.78	11.43	12.47	JANAF	H	1 O	2	0 0 G	0
C2C*CQB	-23.92	87.26	29.78	35.94	41.37	45.92	53.01	58.09	0.00	10/31/96	C	4 H	8 O	2 0 G	4
C*CICCQB	-24.38	90.10	30.23	36.16	41.22	45.79	52.26	57.51	0.00	10/31/96	C	4 H	8 O	2 0 G	4
C*CICCOHB	-38.26	82.01	24.81	30.17	35.04	39.27	46.13	51.21	58.97	10/31/96	C	4 H	8 O	1 0 G	3
C2C*COHB	-45.93	79.05	25.53	31.25	36.25	40.42	46.96	51.79	59.42	10/31/96	C	4 H	8 O	1 0 G	3
C*COHB	-29.61	61.53	14.15	17.32	19.97	22.08	25.19	27.44	31.09	1/ 2/97 THERM	C	2 H	4 O	1 0 G	1
C*CQB	-7.60	69.74	18.40	22.01	25.09	27.58	31.24	33.74	0.00	1/ 2/97 THERM	C	2 H	4 O	2 0 G	2
CC*CB	4.65	63.81	15.45	19.23	22.72	25.79	30.74	34.49	40.39	10/31/96	C	3 H	6	0 0 G	1
C2H4B	12.52	52.47	10.20	12.72	15.02	17.00	20.14	22.54	26.38	10/31/96	C	2 H	4	0 0 G	0
C*COHCB	-38.81	72.59	19.18	23.26	26.77	29.82	34.95	38.72	44.37	10/31/96	C	3 H	6 O	1 0 G	2
C*CQCB	-15.57	82.84	23.59	28.35	32.07	35.40	40.81	44.61	0.00	10/31/96	C	3 H	6 O	2 0 G	3
CC*CQB	-15.47	79.71	23.65	28.52	32.79	36.37	41.84	45.69	0.00	12/25/96 THERM	C	3 H	6 O	2 0 G	3
C*CCQB	-15.93	82.54	24.10	28.74	32.64	36.24	41.09	45.11	0.00	1/18/97 THERM	C	3 H	6 O	2 0 G	3
C*CCOHB	-29.81	74.45	18.68	22.75	26.46	29.72	34.96	38.81	44.65	10/31/96	C	3 H	6 O	1 0 G	2

Table IIA. 3 Thermodynamic Properties for Species in MTBE System (Cont')

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500 DATE	ELEME	N	TS					
CC*COHB	-37.48	71.50	19.40	23.83	27.67	30.87	35.79	39.39	45.10 12/24/96 THERM	C	3	H	6	O	1	0	G 2
CHOC.*O	-19.70	65.41	14.71	16.69	18.05	19.19	21.07	21.91	0.00 4/18/97 THERM	C	2	H	1	O	2	0	G 1
C*CC.*O	10.58	66.00	16.82	20.07	22.49	24.41	27.35	29.39	0.00 4/18/97 THERM	C	3	H	3	O	1	0	G 1

Table IIA. 4 Detailed Mechanism for MTBE Pyrolysis and Oxidation at 1 atm and 300 -20000 K

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04/17/97  mtbe mechanism by ruwei
ELEMENTS
C H O AR N
END
SPECIES
C3COC  CH4  CO  CO2  HCHO  C2H6  C2H4  C2H2  CC*C   CH3OH C2C*C C2C*O  C*CICC*O
OH  HO2  H  O  CH3O  CH3  C2.C*C C*CC.  C2.C*O  CC.C C3.COC  C3COC.  C3C.  H2  O2
H2O  H2O2 C*CICCOH C2C*COH C2CC*O C*CICCQ C2C*CQ C2C*C*O C*CC*O C*CICOC
C2CYCOC C3C C*C*O  C*C*C CC*C*O CC*OC*O C*COHC C*CCOH  C#CC  CCC*O C*CICOOC
C*CYCCOC C3CQ C2CQC*O C2COHC*O YCOCICCQ YCOCICCOH C2CYC2O3 CCYCCOC
OHCYCCOC C*CQC COC CH3CHO  CCOH  C*COH C#COH C*COOC COHCHO COHCQ  COCQ
CH3OOH  CQCHO CC*CQ CC*COH CCQCHO CCOHCHO HCQ*O CQH2OH HCO2H YCOCICQ
YCOCICOH QCYCCOC CQCYCOC CC*OCOH CC*OCQ  CCYCOC QCCQ CYC3OICOH  C*COC
CYCOC C*CQ  QCCHO COHCOH  O*CC*O  C*CCQ  N2  AR C2H5  C2H3  C3CQ.  C3.CQ
C2.COC  C2COC.  C3CO.  C3.COH  C3.C  C2C.OC C2CCO. C2.CCOH C2C.COH C2CC.OH C2CCQ.
C2.CCQ C2C.CQ C2CC.Q C2C.C*O C2CC.*O C2CO.C*O C2CQ.C*O C2.CQC*O C2CQC.*O
C*CICCQ. C*CIC.CQ C*CICC.Q C*CICCO. X Y C2C*CO. C*CICC.*O C2COHCQ. C2CO.CQ
C2.COHCQ C2COHC.Q C2CQ.COH C2.CQCOH C2CQCO. C2CQC.OH C2CQCQ. C2CQ.CQ
C2CQC.Q  C2.CQCQ CCICO.C*O C*CICOOC. CCYC.COOC CCYCC.OOC C2.CYCOOC
C2CYCOOC. YCOCICCO. C2CYCOC.  CYC.OOC C2CQ. C2C.Q  C2.CQ  C.CCQ  CC.CQ  CCC.Q
CCCQ.  C2C.OH  C2CO.  C2.COH C.CCOH  CC.COH CCC.OH  CCCO. CC*CO.  C*CCQ.  C*CC.Q
C*C.CQ  C.*CCQ  C*CCO. C.CQCQ CC.QCQ CCQ.CQ CCQC.Q CCQCQ. C.CQCOH CC.QCOH
CCQ.COH CCQC.OH CCQCO. CC*OCO. CCO.C*O CCOHC.*O O*CCCO. CC.C*O CCC.*O C*CO.C
O*CC.*O C*CC.*O CC.*C  CC*C. CCC.  C*COOC. CCOHCQ. CCO.CQ CCOHC.Q CC.OHCQ
C.COHCQ CCYC.OC CO.CYCOC  YC.COOC YCC.OOC CCYC.OOC C.CYCOOC CCYCOOC.
C*CQ. C.*CQ C.*COH C*CO. CYC.OC C.CHO  CH3C.*O  CCQ. C.CQ  CC.Q C.COH  CCO. CC.OH
CH3OO  CH2OOH CH2  CHO  CH2OH CH2S HCOH COC. O*CCO. HCQ.*O  C.Q*O CQ.H2OH
CQH2O. HOC.HQ  HOCH2O. C.O2H  HCO2.  CO.CQ COHCQ. COHC.Q C.OHCQ  Q.CCHO QC.CHO
QCC.*O CO.COH C.OHCOH  QCCQ. QCC.Q  CO.CHO  C.OHCHO  COHC.*O  COCQ.  COC.Q
C.OCQ C2COHC.*O  CCQC.*O C2C*CB  HO2B C2C*CQB C*CICCQB  C*CICCOHB  C2C*COHB
C*CCOHB CC*COHB  C*COHB  C*CQB  CC*CB  C2H4B  C*COHCB  C*CQCB  C*CCQB
CC*CQB
END
REACTION
O + O + M          <=> O2 + M            1.88E+13   0.00   -1788.    !86
    AR/1./
H + O2 + M         <=> HO2 + M           6.17E+17  -0.80      0.    !92
    AR/1./ N2/2.29/ H2/3.42/ H2O/2.53/
HO2 + HO2          <=> H2O2 + O2         1.87E+12   0.00    1540.    !92
HO2 + O            <=> OH + O2           3.25E+13   0.00      0.    !92
HO2 + H            <=> H2O + O           3.01E+13   0.00    1721.    !92
HO2 + H            <=> H2 + O2           4.28E+13   0.00    1411.    !92
HO2 + H            <=> OH + OH           1.69E+14   0.00     874.    !92
H2O2 + M           <=> OH + OH +M        1.81E+16   0.00   42924.    !92
    AR/1./ N2/6.69/
H2O2 + H           <=> H2 +HO2           1.69E+12   0.00    3756.    !92
H2O2 + H           <=> H2O + OH          1.02E+13   0.00    3577.    !92
H2O2 + O           <=> OH + HO2          6.62E+11   0.00    3974.    !92
H + O + M          <=> OH + M            4.71E+18  -1.00      0.    !86
H + O2             <=> OH + O            1.99E+14   0.00   16812.    !92
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O + H2          <=> OH + H          5.11E+04   2.67    6280.    !92
H + H + M       <=> H2 + M          6.52E+17   -1.00     0.     !92
    AR/1./ N2/1.5/ H2/1.47/
OH + OH         <=> O + H2O         1.51E+09   1.14     99     !92
OH + H + M      <=> H2O + M         8.35E+21   -2.00     0.    !92
    AR/1./ N2/2.65/  H2O/16.91/
OH + H2         <=> H2O + H         1.02E+08   1.60    3299.   !92
OH + HO2        <=> H2O + O2        2.89E+13   0.00    -497.   !92
OH + H2O2       <=> HO2 + H2O       7.83E+12   0.00    1331.   !92
HO2             => X + Y            1.00E+00   0.00     0.     !
H2O2            => H2O + X          1.00E+00   0.00     0.     !
X + X           => O2               1.00E+15   0.00     0.     !
X + Y + Y       => H2O + O2         1.00E+19   0.00     0.     !
C3COC + H       <=> C3.COC + H2     2.16E+09   1.50    6997.   !F
C3COC + H       <=> C3COC. + H2     7.20E+08   1.50    4352.   !F
C3COC + O       <=> C3.COC + OH     1.53E+09   1.50    5305.   !F
C3COC + O       <=> C3COC. + OH     5.35E+12   0.00    3031.   !n
C3COC + OH      <=> C3.COC + H2O    1.08E+07   2.00     525.   !F
C3COC + OH      <=> C3COC. + H2O    6.27E+12   0.00     739.   !8
C3COC + CH3     <=> C3.COC + CH4    1.36E+00   3.65    7154.   !9
C3COC + CH3     <=> C3COC. + CH4    1.31E+00   4.00   11567.   !b
C3COC + CH3O    <=> C3.COC + CH3OH  9.03E+11   0.00    7866.   !b
C3COC + CH3O    <=> C3COC. + CH3OH  3.01E+11   0.00    5266.   !A
C3COC + HO2     <=> C3.COC + H2O2   3.01E+04   2.55   15500.   !9
C3COC + HO2     <=> C3COC. + H2O2   9.64E+10   0.00   12536.   !8
C3COC + O2      <=> C3COC. + HO2    2.05E+13   0.00   38392.   !8
C3COC + O2      <=> C3.COC + HO2    4.04E+13   0.00   39432.   !9
C3C. + CH3O     <=> C3COC           0.00E+00    .000     0. ! mtbe017d.mec avg err  .00%
C3C. + CH3O     <=> C2C*C + CH3OH   9.19E+37  -7.839   8102. ! mtbe017d.mec avg err
47.78%
C3C. + CH3O     <=> C3CO. + CH3     8.72E+05   2.448   7526. ! mtbe017d.mec avg err
112.73%
C3C. + CH3O     <=> C2C.OC + CH3    1.11E+02   3.529  11971. ! mtbe017d.mec avg err
123.04%
C3C. + CH3O     <=> C3.COC + H      7.94E+14   -.786  14903. ! mtbe017d.mec avg err 137.13%
C3C. + CH3O     <=> C3COC. + H      1.50E+06   2.144  27290. ! mtbe017d.mec avg err 74.97%
C3COC           <=> C2C*C + CH3OH   5.35E+03   2.575  23829. ! mtbe017d.mec avg err
85.74%
C3COC           <=> C2C.OC + CH3    3.68E+24  -3.237  60518. ! mtbe017d.mec avg err 42.37%
C3COC           <=> C3.COC + H      2.79E+53 -12.065  90110. ! mtbe017d.mec avg err 56.49%
C3COC           <=> C3COC. + H      4.33E+47  -9.999 109503. ! mtbe017d.mec avg err 36.96%
C3CO. + CH3     <=> C3COC           2.06E+45  -9.593 105188. ! mtbe017d.mec avg err 39.82%
C3CO. + CH3     <=> C2C*C + CH3OH   1.09E+37  -7.502   7800. ! mtbe017d.mec avg err
48.10%
C3CO. + CH3     <=> C2C.OC + CH3    5.46E+04   2.863   7524. ! mtbe017d.mec avg err
118.30%
C3CO. + CH3     <=> C3.COC + H      1.98E+15   -.825  16219. ! mtbe017d.mec avg err 139.60%
C3CO. + CH3     <=> C3COC. + H      7.37E+07   1.736  29651. ! mtbe017d.mec avg err 74.01%
C3.COC          <=> C2C*C + CH3O    1.77E+05   2.216  26030. ! mtbe017d.mec avg err 84.87%
C3.COC          <=> C*CICOC + CH3   2.45E+36  -7.795  30284. ! mtbe017d.mec avg err  9.77%
C3.COC          <=> C3COC.          1.09E+37  -7.751  32131. ! mtbe017d.mec avg err  9.08%
C3.COC          <=> C3C. + HCHO     4.46E+38  -9.316  23904. ! mtbe017d.mec avg err  6.23%
C3COC.          <=> C2C*C + CH3O    7.89E+37  -8.217  28428. ! mtbe017d.mec avg err 18.17%
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C3COC.          <=> C*CICOC + CH3      3.38E+30  -6.142  36763. ! mtbe017d.mec avg err
11.35%
C3COC.          <=> C3C. + HCHO        3.45E+30  -5.918  37994. ! mtbe017d.mec avg err  8.38%
C2.COC          <=> CC*C + CH3O        6.16E+28  -5.722  15530. ! mtbe017d.mec avg err 26.07%
C2.COC          <=> C*COC + CH3        5.55E+33  -7.097  28720. ! mtbe017d.mec avg err 13.00%
C2.COC          <=> C*CICOC + H        9.35E+32  -6.801  31665. ! mtbe017d.mec avg err 15.60%
C2.COC          <=> C2COC.             7.10E+30  -6.270  34832. ! mtbe017d.mec avg err 18.43%
C2.COC          <=> CC.C + HCHO        1.70E+41  -9.848  25315. ! mtbe017d.mec avg err  6.43%
C2.COC          <=> C2C.OC             1.21E+37  -7.921  28402. ! mtbe017d.mec avg err 20.12%
C2.COC          <=> C2C*O + CH3        2.39E+21  -4.599  36248. ! mtbe017d.mec avg err 34.60%
C2COC.          <=> CC.C + HCHO        1.10E+26  -4.792  39364. ! mtbe017d.mec avg err 22.45%
C2COC.          <=> CCYCOC + CH3       1.37E+50 -12.388  24373. ! mtbe017d.mec avg err
38.54%
C2COC.          <=> C2C.OC             4.95E+65 -18.009  45221. ! mtbe017d.mec avg err 31.65%
C2C.OC          <=> C2C*O + CH3        6.26E+32  -9.952  13418. ! mtbe017d.mec avg err 34.51%
C2C.OC          <=> C*CICOC + H        2.06E+34  -7.809  11603. ! mtbe017d.mec avg err 27.25%
C3C. + C3COC      <=> C3.COC + C3C     5.06E-06   5.17   9068.   !90
C3C. + C3COC      <=> C3COC. + C3C     7.84E-05   4.70   9320.   !A
C3C. + CH3OH      <=> C3C + CH3O       1.50E+03   1.80   9358.   !90T
C3C. + CH3OH      <=> C3C + CH2OH      7.84E-05   4.70   9085.   !90
C3C. + HCHO       <=> C3C + CHO        3.25E+09   0.00   3553.   !90
C3C. + C2C*O      <=> C3C + C2.C*O     6.02E-05   4.90  11362.   !A
C3C. + C2C*C      <=> C3C + C2.C*C     6.02E-05   4.90   8362.   !2*
C3C. + CC*C       <=> C3C + C*CC.      3.01E-05   4.90   8362.   !91
C3C. + O2         <=> C2C*C + HO2      4.82E+11   0.00      0.   !90
C3C. + C2CYCOC    <=> C3C + C2CYCOC.   1.07E+11   0.00  11832.   !1/
C3C. + CCYCOC     <=> C3C + CCYC.OC    5.06E-06   5.17   9068.   !90
C3C. + C*CICC*O   <=> C3C + C*CICC.*O  1.02E+10   0.00   6838.   !85
C3C. + C2CC*O     <=> C3C + C2CC.*O    4.00E+10   0.00   6299.   !1/
C3C. + O*CC*O     <=> C3C + O*CC.*O    2.16E+10   0.00   6955.   !1/
C3C. + CCC*O      <=> C3C + CCC.*O     1.08E+10   0.00   6955.   !1/
C3C. + CH3CHO     <=> C3C + CH3C.*O    1.08E+10   0.00   6955.   !1/
C3C. + C2CQC*O    <=> C3C + C2CQC.*O   5.40E+09   0.00   6955.   !1/
C3C. + C2COHC*O   <=> C3C + C2COHC.*O  5.40E+09   0.00   6955.   !1/
C3C. + CCQCHO     <=> C3C + CCQC.*O    5.40E+09   0.00   6955.   !1/
C3C. + CCOHCHO    <=> C3C + CCOHC.*O   5.40E+09   0.00   6955.   !1/
C2C*C + H       <=> C3C.           3.08E+62 -17.123  50708. ! mtbe017d.mec avg err 39.04%
C2C*C + H       <=> C3.C           4.80E+38  -7.952  11164. ! mtbe017d.mec avg err 39.56%
C2C*C + H       <=> CC*C + CH3     5.78E+35  -7.003  21804. ! mtbe017d.mec avg err 43.70%
C3C.          <=> C3.C           2.44E+21  -1.801  22816. ! mtbe017d.mec avg err 55.38%
C3C.          <=> CC*C + CH3     2.16E+60 -14.925  58325. ! mtbe017d.mec avg err 37.88%
C3.C          <=> CC*C + CH3     1.97E+49 -11.006  59961. ! mtbe017d.mec avg err 61.28%
C3C. + O2       <=> C3CQ.          6.32E+65 -16.876  45250. ! mtbe017d.mec avg err 51.90%
C3C. + O2       <=> C2C*CB + HO2B  1.42E+52 -13.155  10033. ! mtbe017d.mec avg err
29.43%
C3C. + O2       <=> C3CO. + O      4.19E+22  -2.930  10487. ! mtbe017d.mec avg err 10.29%
C3C. + O2       <=> C3.CQ          5.45E+15  -1.025  27929. ! mtbe017d.mec avg err  2.02%
C3C. + O2       <=> C2C*C + HO2    3.41E+36  -8.154   9841. ! mtbe017d.mec avg err 16.15%
C3C. + O2       <=> C2CYCOC + OH   3.07E+32  -5.908  13002. ! mtbe017d.mec avg err
14.48%
C3C. + O2       <=> C*CQC + CH3    9.43E+23  -3.796  13191. ! mtbe017d.mec avg err 10.01%
C3CQ.         <=> C2C*CB + HO2B  1.88E+14   -.629  19932. ! mtbe017d.mec avg err  2.84%
C3CQ.         <=> C3CO. + O      4.52E+50 -11.762  42106. ! mtbe017d.mec avg err 28.99%
C3CQ.         <=> C3.CQ          7.95E+32  -6.762  60220. ! mtbe017d.mec avg err 39.21%
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C3CQ.          <=> C2CYCOC + OH      6.20E-65 -16.937  41407. ! mtbe017d.mec avg err
11.75%
C3CQ.          <=> C*CQC + CH3       5.27E-52 -12.828  45984. ! mtbe017d.mec avg err 35.22%
C3.CQ          <=> C2CYCOC + OH      6.72E+34  -7.336  52167. ! mtbe017d.mec avg err 39.07%
C3.CQ          <=> C*CQC + CH3       6.22E+20  -3.690  19206. ! mtbe017d.mec avg err 27.50%
C*CQC          <=> C*CO.C + OH       2.04E+14  -1.342  32073. ! mtbe017d.mec avg err 21.66%
C2C*C + O      <=> C2.C*C + OH       1.21E+11   0.70   7633. !2*91T
C2C*C + O      <=> C2CYCOC           4.20E+12   0.00    503. !73HER
C2C*C + H      <=> C2.C*C + H2       3.50E+05   2.50   2492. !2*91T
C2C*C + H      <=> CC*C + CH3        1.45E+13   0.00   1302. !2*91T
C2C*C + OH     <=> C2.C*C + H2O      6.24E+06   2.00   -298. !91TSA
C2C*C + CH3    <=> C2.C*C + CH4      4.42E+00   3.50   5675. !2*(ch
C2C*C + CH3O   <=> C2.C*C + CH3OH    4.42E+00   3.50   5675. !take
C2C*C + HO2    <=> C2.C*C + H2O2     1.93E+04   2.60  13910. !2*91T
C2C*C + HO2    <=> C2CYCOC + OH      1.05E+12   0.00  14206. !91TSA
C2C*C + O2     <=> C2.C*C + HO2      4.79E+12   0.00  38560. !R.W.W
C2C*C          <=> CC.*C + CH3       5.84E+39  -8.950  23050 ! mtbe017d.mec avg err 38.90%
CC.*C          <=> C*C*C + H         9.85E+35  -5.826 103757. ! mtbe017d.mec avg err 59.26%
CC*C           <=> C*CC.             8.75E+43 -10.144  47445. ! mtbe017d.mec avg err 15.84%
C2C*C + HO2    <=> C3.CQ             1.96E+41  -8.892  43223. ! mtbe017d.mec avg err 27.93%
C2C*C + HO2    <=> C2CYCOC + OH      3.76E+17  -2.102  10117. ! mtbe017d.mec avg err
30.26%
C2C*C + HO2    <=> C*CQC + CH3       2.39E+05   2.304  17411. ! mtbe017d.mec avg err
3.45%
C2C*C + HO2    <=> C3CQ.             3.50E+03   3.274  30182. ! mtbe017d.mec avg err  .59%
C2C*C + HO2    <=> C3CO. + O         3.36E+47 -11.249  24700. ! mtbe017d.mec avg err
35.68%
C2C*C + HO2    <=> C2C.CQ            5.72E+04   2.665  40446. ! mtbe017d.mec avg err  5.63%
C2C*C + HO2    <=> C2CYCOC + OH      3.49E+23  -3.964  11471. ! mtbe017d.mec avg err
22.26%
C2C*C + HO2    <=> C*CICCQ + H       2.96E+09   1.000  19237. ! mtbe017d.mec avg err
6.05%
C2C*C + HO2    <=> C2C*CQ + H        1.18E+10   1.174  34521. ! mtbe017d.mec avg err
2.81%
C2C*C + HO2    <=> C2CCQ.            2.39E+08   1.222  36450. ! mtbe017d.mec avg err  2.67%
C2C*C + HO2    <=> C3.C + O2         1.24E+40  -8.945  26000. ! mtbe017d.mec avg err 21.38%
C2C*C + HO2    <=> C2.CCQ            2.94E+23  -2.934  31462. ! mtbe017d.mec avg err 19.55%
C2C*C + HO2    <=> CCYCCOC + OH      3.04E+36  -7.380  31559. ! mtbe017d.mec avg err
38.79%
C2C*C + HO2    <=> CC*C + CH2OOH     1.84E+31  -5.618  36765. ! mtbe017d.mec avg err
28.92%
C2C*C + HO2    <=> C*CCQ + CH3       1.04E+25  -3.229  42362. ! mtbe017d.mec avg err
12.84%
C2C*C + HO2    <=> C2CC.Q            3.72E+24  -3.282  42181. ! mtbe017d.mec avg err 13.04%
C2C*C + HO2    <=> C2CC*O + OH       1.31E+09   -.189  37137. ! mtbe017d.mec avg err
6.39%
C2C*C + HO2    <=> CC*CQ + CH3       1.65E+12   .058  38011. ! mtbe017d.mec avg err
9.08%
C2C.CQ         <=> C2CYCOC + OH      1.56E-16   7.523  37817. ! mtbe017d.mec avg err  4.45%
C2C.CQ         <=> C*CICCQ + H       2.73E+22  -4.076  21392. ! mtbe017d.mec avg err 24.42%
C2C.CQ         <=> C2C*CQ + H        5.07E+18  -2.626  36845. ! mtbe017d.mec avg err 20.23%
C2C.CQ         <=> C2C*CB + HO2B     4.84E+16  -2.483  38765. ! mtbe017d.mec avg err
20.17%
C2C.CQ         <=> C3.C + O2         2.97E+32  -7.274  31426. ! mtbe017d.mec avg err 12.88%
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```
C2C.CQ          <=> C2.CCQ          3.44E+33  -7.109  33506. ! mtbe017d.mec avg err  9.14%
C2C.CQ          <=> CCYCCOC - OH      4.60E+45 -11.196  32769. ! mtbe017d.mec avg err
29.38%
C2C.CQ          <=> CC*C + CH2OOH     6.47E+39  -9.317  38266. ! mtbe017d.mec avg err
14.49%
C2C.CQ          <=> C*CCQ + CH3       5.04E+32  -6.701  44363. ! mtbe017d.mec avg err  5.06%
C2C.CQ          <=> C2CC.Q          1.99E+32  -6.766  44185. ! mtbe017d.mec avg err  4.99%
C2C.CQ          <=> C2CC*O + OH       1.19E+18  -4.055  39608. ! mtbe017d.mec avg err 10.95%
C2C.CQ          <=> CC*CQ + CH3       1.35E+21  -3.800  40448. ! mtbe017d.mec avg err 15.80%
C2CCQ.          <=> C2C.CQ          7.88E-10   4.250  39421. ! mtbe017d.mec avg err 13.42%
C2CCQ.          <=> C2CYCOC + OH      1.00E+54 -13.631  35442. ! mtbe017d.mec avg err
6.86%
C2CCQ.          <=> C2C*CB + HO2B     1.46E+44 -10.268  42304. ! mtbe017d.mec avg err
20.48%
C2CCQ.          <=> C3.C + O2         1.66E+41  -9.381  35539. ! mtbe017d.mec avg err 16.14%
C2CCQ.          <=> C2.CCQ          8.78E+44  -9.980  39863. ! mtbe017d.mec avg err 16.19%
C2CCQ.          <=> CCYCCOC + OH      3.38E+49 -11.846  33357. ! mtbe017d.mec avg err
30.38%
C2CCQ.          <=> CC*C + CH2OOH     1.69E+49 -11.588  43703. ! mtbe017d.mec avg err
17.24%
C2CCQ.          <=> C*CCQ + CH3       2.91E+44  -9.661  52348. ! mtbe017d.mec avg err 14.82%
C2CCQ.          <=> C*CICCQ + H       1.14E+44  -9.724  52143. ! mtbe017d.mec avg err 14.71%
C2CCQ.          <=> C2CC.Q          2.30E+40  -9.234  54127. ! mtbe017d.mec avg err 15.93%
C2CCQ.          <=> C2CC*O + OH       1.02E+31  -7.369  48089. ! mtbe017d.mec avg err 21.16%
C2CCQ.          <=> CC*CQ + CH3       1.12E+34  -7.115  48912. ! mtbe017d.mec avg err 27.34%
C2CCQ.          <=> C2C*CQ + H        2.10E+02   1.319  47418. ! mtbe017d.mec avg err 24.63%
C2.CCQ          <=> CCYCCOC + OH      3.02E-02   2.178  49534. ! mtbe017d.mec avg err
23.96%
C2.CCQ          <=> CC*C + CH2OOH     7.83E+23  -4.387  19296. ! mtbe017d.mec avg err
17.98%
C2.CCQ          <=> C*CCQ + CH3       1.82E+25  -4.090  31884. ! mtbe017d.mec avg err 12.21%
C2.CCQ          <=> C*CICCQ + H       4.95E+24  -4.111  31597. ! mtbe017d.mec avg err 12.23%
C2.CCQ          <=> C2CC.Q          2.56E+22  -4.008  34297. ! mtbe017d.mec avg err 11.47%
C2.CCQ          <=> C2CC*O + OH       3.35E+25  -5.957  36196. ! mtbe017d.mec avg err  8.00%
C2CC.Q          <=> C2CC*O + OH       6.14E+28  -5.766  37106. ! mtbe017d.mec avg err  3.48%
C2CC.Q          <=> CC*CQ + CH3       2.10E+08   .188   -837. ! mtbe017d.mec avg err  4.31%
C2CC.Q          <=> C2C*CQ + H        5.51E+08  -.020  33294. ! mtbe017d.mec avg err  5.34%
C3.CQ + O2       <=> C2CQCQ.          7.49E+07   .027  38424. ! mtbe017d.mec avg err  5.55%
C3.CQ + O2       <=> C2CQ.CQ          9.80E+37  -8.502   6836. ! mtbe017d.mec avg err  4.58%
C3.CQ + O2       <=> C2C.CQ + O2       5.81E+70 -19.203  19968. ! mtbe017d.mec avg err
46.38%
C3.CQ + O2       <=> C*CICCQB + HO2B    1.47E+60 -15.155  25775. ! mtbe017d.mec avg err
34.46%
C3.CQ + O2       <=> C2C*CQB + HO2B     2.15E+54 -13.464  26099. ! mtbe017d.mec avg err
31.64%
C3.CQ + O2       <=> C2.CQCQ          1.85E+53 -13.306  26221. ! mtbe017d.mec avg err 30.65%
C3.CQ + O2       <=> C*CICCQ + HO2      3.89E+40  -9.229  12322. ! mtbe017d.mec avg err
10.11%
C3.CQ + O2       <=> C*CQC + CH2OOH     1.26E+34  -6.295  15389. ! mtbe017d.mec avg err
16.35%
C3.CQ + O2       <=> YCOCICCQ + OH      1.34E+20  -2.150  24004. ! mtbe017d.mec avg err
7.26%
C3.CQ + O2       <=> C2CQC.Q          8.35E+27  -5.088  16160. ! mtbe017d.mec avg err 13.78%
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```
C3.CQ + O2      <=> C2C*CQ + HO2      7.60E+11  -1.503  18640. ! mtbe017d.mec avg err
5.90%
C3.CQ + O2      <=> C2CQC*O + OH      2.52E-02   3.158  18661. ! mtbe017d.mec avg err
3.02%
C2CQCQ.         <=> C2CQ.CQ          4.75E+13   -.810  18816. ! mtbe017d.mec avg err  5.89%
C2CQCQ.         <=> C*CICCQB + HO2B   1.05E+52 -13.673  24146. ! mtbe017d.mec avg err
93.78%
C2CQCQ.         <=> C2C*CQB + HO2B    1.47E+68 -17.595  53716. ! mtbe017d.mec avg err
44.61%
C2CQCQ.         <=> C2.CQCQ          3.25E+67 -17.561  54145. ! mtbe017d.mec avg err 41.77%
C2CQCQ.         <=> C*CICCQ + HO2     4.53E+57 -14.360  35251. ! mtbe017d.mec avg err
42.22%
C2CQCQ.         <=> C*CQC + CH2OOH    2.38E+54 -12.489  43089. ! mtbe017d.mec avg err
7.57%
C2CQCQ.         <=> YCOCICCQ + OH     3.33E+34  -6.663  53808. ! mtbe017d.mec avg err
10.85%
C2CQCQ.         <=> C2CQC.Q          1.29E+48 -11.271  44973. ! mtbe017d.mec avg err  6.70%
C2CQCQ.         <=> C2C*CQ + HO2      1.49E+27  -6.305  47767. ! mtbe017d.mec avg err
4.99%
C2CQCQ.         <=> C2CQC*O + OH      4.94E+09   -.561  46332. ! mtbe017d.mec avg err
9.36%
C2CQ.CQ         <=> C*CICCQB + HO2B   4.33E+28  -5.527  47800. ! mtbe017d.mec avg err
7.61%
C2CQ.CQ         <=> C2C*CQB + HO2B    1.34E+44  -9.366  46784. ! mtbe017d.mec avg err
21.02%
C2CQ.CQ         <=> C2.CQCQ          3.59E+43  -9.351  47334. ! mtbe017d.mec avg err 19.28%
C2CQ.CQ         <=> C*CICCQ + HO2     2.44E+74 -19.964  47739. ! mtbe017d.mec avg err
85.53%
C2CQ.CQ         <=> C*CQC + CH2OOH    1.46E+81 -21.260  57766. ! mtbe017d.mec avg err
45.15%
C2CQ.CQ         <=> YCOCICCQ + OH     2.19E+63 -16.455  66307. ! mtbe017d.mec avg err
8.02%
C2CQ.CQ         <=> C2CQC.Q          3.57E+77 -20.910  60035. ! mtbe017d.mec avg err 32.89%
C2CQ.CQ         <=> C2C*CQ + HO2      1.03E+59 -16.931  61933. ! mtbe017d.mec avg err
11.15%
C2CQ.CQ         <=> C2CQC*O + OH      1.14E+41 -11.203  59537. ! mtbe017d.mec avg err
12.09%
C2.CQCQ         <=> C*CICCQ + HO2     4.52E+60 -16.222  61952. ! mtbe017d.mec avg err
6.52%
C2.CQCQ         <=> C*CQC + CH2OOH    5.23E+31  -6.340  19075. ! mtbe017d.mec avg err
3.53%
C2.CQCQ         <=> YCOCICCQ + OH     4.19E+19  -2.569  35048. ! mtbe017d.mec avg err
9.71%
C2.CQCQ         <=> C2CQC.Q          2.37E+26  -5.329  22018. ! mtbe017d.mec avg err  4.03%
C2CQC.Q         <=> C2C*CQ + HO2B     3.40E+21  -5.249  35383. ! mtbe017d.mec avg err
1.77%
C2CQC.Q         <=> C2CQC*O + OH      2.62E+11   -.768  20933. ! mtbe017d.mec avg err
6.33%
C2C.CQ + O2      <=> C2CQ.CQ          6.68E+09   -.197   -194. ! mtbe017d.mec avg err  6.86%
C2C.CQ + O2      <=> C*CICCQB + HO2B   5.36E+46 -11.225   9319. ! mtbe017d.mec avg err
8.39%
C2C.CQ + O2      <=> C2C*CQB + HO2B    1.62E+25  -3.710  14978. ! mtbe017d.mec avg err
15.31%
C2C.CQ + O2      <=> C2.CQCQ          1.89E+24  -3.585  15193. ! mtbe017d.mec avg err 14.92%
```

```
C2C.CQ + O2      <=> C*CICCQ + HO2      1.07E+41  -9.357  13671. ! mtbe017d.mec avg err
9.02%
C2C.CQ + O2      <=> C*CQC + CH2OOH     3.96E+37  -7.264  17826. ! mtbe017d.mec avg err
20.32%
C2C.CQ + O2      <=> YCOCICCQ + OH      1.28E-23  -2.983  25593. ! mtbe017d.mec avg err
14.03%
C2C.CQ + O2      <=> C2CQC.Q          1.12E+31  -5.954  18245. ! mtbe017d.mec avg err 17.19%
C2C.CQ + O2      <=> C2C*CQ + HO2       6.11E-29  -6.368  12889. ! mtbe017d.mec avg err
23.51%
C2C.CQ + O2      <=> C2CQC*O + OH       8.89E-13  -1.040  13879. ! mtbe017d.mec avg err
14.00%
C2C.CQ + O2      <=> C2CQCQ.          1.74E+31  -5.581  13069. ! mtbe017d.mec avg err 21.34%
C2C*C + OH       <=> C3.COH           1.30E+69 -18.667  20099. ! mtbe017d.mec avg err 47.86%
C2C*C + OH       <=> C*COHC + CH3       1.01E+40  -8.842   8454. ! mtbe017d.mec avg err
18.61%
C2C*C + OH       <=> C3CO.            3.45E+22  -2.806  10906. ! mtbe017d.mec avg err 37.68%
C2C*C + OH       <=> C2C*O + CH3        1.26E+04   .408  13428. ! mtbe017d.mec avg err 2.65%
C3.COH         <=> C*COHC + CH3       7.56E+09   .370  16888. ! mtbe017d.mec avg err 13.56%
C3.COH         <=> C3CO.            4.92E+38  -8.314  34846. ! mtbe017d.mec avg err 20.00%
C3.COH         <=> C2C*O + CH3        6.91E+23  -6.137  42635. ! mtbe017d.mec avg err 25.99%
C3CO.          <=> C2C*O + CH3        1.34E+29  -6.084  45757. ! mtbe017d.mec avg err 21.46%
C2C*C + OH       <=> C2C.COH          6.35E+41 -10.227  13555. ! mtbe017d.mec avg err 36.50%
C2C*C + OH       <=> C*CICCOH + H       1.67E+41  -9.197   8473. ! mtbe017d.mec avg err
21.16%
C2C*C + OH       <=> C2C*COH + H        2.58E+21  -2.329  16684. ! mtbe017d.mec avg err
19.52%
C2C*C + OH       <=> C2.CCOH          4.64E+20  -2.549  13685. ! mtbe017d.mec avg err 29.23%
C2C*C + OH       <=> C*CCOH + CH3       4.68E+39  -8.353  27423. ! mtbe017d.mec avg err
24.29%
C2C*C + OH       <=> C2CC.OH          3.67E+22  -2.520  28201. ! mtbe017d.mec avg err 44.39%
C2C*C + OH       <=> CC*COH + CH3       1.24E+39  -8.531  24554. ! mtbe017d.mec avg err
22.48%
C2C*C + OH       <=> C2CCO.           2.40E+22  -2.655  24698. ! mtbe017d.mec avg err 31.89%
C2C*C + OH       <=> CC.C + HCHO        6.16E+11  -1.395  17916. ! mtbe017d.mec avg err
12.30%
C2C.COH        <=> C*CICCOH + H       2.95E+11   .142  20823. ! mtbe017d.mec avg err
10.46%
C2C.COH        <=> C2C*COH + H        1.18E+41  -8.928  45062. ! mtbe017d.mec avg err
16.30%
C2C.COH        <=> C2.CCOH          1.86E+40  -9.110  41051. ! mtbe017d.mec avg err 17.04%
C2C.COH        <=> C*CCOH + CH3       1.35E+53 -12.959  55072. ! mtbe017d.mec avg err
20.04%
C2C.COH        <=> C2CC.OH          1.03E+36  -7.302  55406. ! mtbe017d.mec avg err 24.38%
C2C.COH        <=> CC*COH + CH3       1.57E+55 -13.870  52766. ! mtbe017d.mec avg err
23.28%
C2C.COH        <=> C2CCO.           7.93E+38  -8.321  52522. ! mtbe017d.mec avg err 23.09%
C2C.COH        <=> CC.C + HCHO        3.61E+30  -7.678  47115. ! mtbe017d.mec avg err
37.53%
C2.CCOH        <=> C*CICCOH + H       2.74E+29  -5.987  49451. ! mtbe017d.mec avg err
19.65%
C2.CCOH        <=> C*CCOH + CH3       3.26E+70 -19.346  49022. ! mtbe017d.mec avg err
52.96%
C2.CCOH        <=> C2CC.OH          8.32E+68 -18.083  45720. ! mtbe017d.mec avg err 62.19%
```

```
C2.CCOH          <=> CC*COH + CH3       1.12E+72 -21.191  38378. ! mtbe017d.mec avg err
28.39%
C2.CCOH          <=> C2CCO.             1.75E+66 -19.475  41279. ! mtbe017d.mec avg err 10.54%
C2.CCOH          <=> CC.C + HCHO        8.96E+63 -18.989  36478. ! mtbe017d.mec avg err
17.34%
C2CC.OH          <=> CC*COH + CH3       5.94E+69 -19.792  40824. ! mtbe017d.mec avg err
8.16%
C2CC.OH          <=> C2C*COH + H        1.22E+39  -8.306  36478. ! mtbe017d.mec avg err
19.62%
C2CC.OH          <=> C2CCO.             1.03E+39  -8.582  41456. ! mtbe017d.mec avg err 17.20%
C2CC.OH          <=> CC.C + HCHO        4.09E+18  -4.410  51680. ! mtbe017d.mec avg err
32.53%
C2CCO.           <=> C*CCOH + CH3       9.96E+19  -3.400  55081. ! mtbe017d.mec avg err
20.25%
C2CCO.           <=> CC*COH + CH3       1.00E+59 -18.253  38985. ! mtbe017d.mec avg err
26.48%
C2CCO.           <=> CC.C + HCHO        2.51E+53 -15.167  31250. ! mtbe017d.mec avg err 45.59%
C3.COH + O2      <=> C2COHCQ.           7.75E+54 -14.011  22709. ! mtbe017d.mec avg err
19.86%
C3.COH + O2      <=> C2CO.CQ            9.36E+37  -8.428   7106. ! mtbe017d.mec avg err  6.03%
C3.COH + O2      <=> C2C*O + CH2OOH     7.63E+38  -9.475  11260. ! mtbe017d.mec avg err
30.80%
C3.COH + O2      <=> C2.COHCQ           5.02E+31  -6.021  11292. ! mtbe017d.mec avg err
24.48%
C3.COH + O2      <=> C*CICCQ + OH       9.52E+39  -8.882  13278. ! mtbe017d.mec avg err
30.43%
C3.COH + O2      <=> C*COHC + CH2OOH    1.18E+31  -5.404  24465. ! mtbe017d.mec avg err
16.11%
C3.COH + O2      <=> CYC3OICOH + OH     1.15E+32  -5.703  23025. ! mtbe017d.mec avg err
18.26%
C3.COH + O2      <=> C2COHC.Q           3.19E+36  -7.476  18531. ! mtbe017d.mec avg err
27.71%
C3.COH + O2      <=> C2C*CQ + OH        1.15E+13  -1.427  18296. ! mtbe017d.mec avg err
9.48%
C3.COH + O2      <=> C2COHC*O + OH      4.04E-11   5.981  20550. ! mtbe017d.mec avg err
5.91%
C2COHCQ.         <=> C2CO.CQ            3.49E+15  -1.087  19026. ! mtbe017d.mec avg err  7.95%
C2COHCQ.         <=> C2C*O + CH2OOH     3.15E+52 -13.831  28007. ! mtbe017d.mec avg err
23.55%
C2COHCQ.         <=> C2.COHCQ           7.88E+46 -10.843  33914. ! mtbe017d.mec avg err
8.96%
C2COHCQ.         <=> C*CICCQ + OH       9.11E+46 -11.220  32002. ! mtbe017d.mec avg err
33.41%
C2COHCQ.         <=> C*COHC + CH2OOH    1.52E+43  -9.303  52862. ! mtbe017d.mec avg err
5.32%
C2COHCQ.         <=> CYC3OICOH + OH     2.69E+44  -9.671  51060. ! mtbe017d.mec avg err
4.88%
C2COHCQ.         <=> C2COHC.Q           5.69E+46 -10.810  42579. ! mtbe017d.mec avg err
17.42%
C2COHCQ.         <=> C2C*CQ + OH        5.80E+28  -6.436  47807. ! mtbe017d.mec avg err
6.72%
C2COHCQ.         <=> C2COHC*O + OH      1.47E+00   2.316  48558. ! mtbe017d.mec avg err
18.77%
```

```
C2CO.CQ          <=> C2C*O + CH2OOH     1.20E+31  -6.061  48440. ! mtbe017d.mec avg err
12.98%
C2CO.CQ          <=> C2.COHCQ           1.40E+27  -5.079  10911. ! mtbe017d.mec avg err 13.93%
C2CO.CQ          <=> C*CICCQ + OH       2.07E+50 -12.999  22206. ! mtbe017d.mec avg err
43.49%
C2CO.CQ          <=> C*COHC + CH2OOH    1.41E+42  -9.747  41124. ! mtbe017d.mec avg err
18.58%
C2CO.CQ          <=> CYC3OICOH + OH     2.24E+43 -10.107  39286. ! mtbe017d.mec avg err
21.03%
C2CO.CQ          <=> C2COHC.Q           2.66E+45 -11.203  30472. ! mtbe017d.mec avg err 41.47%
C2CO.CQ          <=> C2C*CQ + OH        1.40E+27  -6.699  35868. ! mtbe017d.mec avg err
16.75%
C2CO.CQ          <=> C2COHC*O + OH      1.02E-02   2.260  36560. ! mtbe017d.mec avg err
8.73%
C2.COHCQ         <=> C2C*O + CH2OOH     2.50E+29  -6.303  36488. ! mtbe017d.mec avg err
17.26%
C2.COHCQ         <=> C*CICCQ + OH       7.87E+43 -10.184  26797. ! mtbe017d.mec avg err
35.33%
C2.COHCQ         <=> C*COHC + CH2OOH    2.43E+26  -4.455  33296. ! mtbe017d.mec avg err
13.04%
C2.COHCQ         <=> CYC3OICOH + OH     2.79E+26  -4.502  30768. ! mtbe017d.mec avg err
13.70%
C2.COHCQ         <=> C2COHC.Q           2.03E+25  -4.790  19260. ! mtbe017d.mec avg err
14.40%
C2.COHCQ         <=> C2C*CQ + OH        1.67E+28  -6.558  38162. ! mtbe017d.mec avg err
13.86%
C2.COHCQ         <=> C2COHC*O + OH      2.78E+03   1.043  39759. ! mtbe017d.mec avg err
4.23%
C2COHC.Q         <=> C2C*O + CH2OOH     5.60E+30  -6.244  38874. ! mtbe017d.mec avg err
7.83%
C2COHC.Q         <=> C*CICCQ + OH       6.23E-05   2.284  10221. ! mtbe017d.mec avg err
92.10%
C2COHC.Q         <=> C*COHC + CH2OOH    8.52E+13  -1.786  47668. ! mtbe017d.mec avg err
11.43%
C2COHC.Q         <=> CYC3OICOH + OH     7.39E-24   8.452  15822. ! mtbe017d.mec avg err
88.21%
C2COHC.Q         <=> C2C*CQ + OH        1.06E+29  -7.724  22510. ! mtbe017d.mec avg err
100.90%
C2COHC.Q         <=> C2COHC*O + OH      9.08E+10   -.445  35847. ! mtbe017d.mec avg err
4.16%
C2C.COH + O2     <=> C2CQ.COH           4.95E+09   -.203   -356. ! mtbe017d.mec avg err 2.74%
C2C.COH + O2     <=> C*CICCOHB + HO2B   3.63E+46 -11.322   8598. ! mtbe017d.mec avg err
17.25%
C2C.COH + O2     <=> C2C*COHB + HO2B    8.67E+21  -2.724  12791. ! mtbe017d.mec avg err
9.68%
C2C.COH + O2     <=> C2.CQCOH           9.98E+27  -4.525  11315. ! mtbe017d.mec avg err
14.64%
C2C.COH + O2     <=> C*CICCOH + HO2     2.29E+41  -9.750  12643. ! mtbe017d.mec avg err
21.59%
C2C.COH + O2     <=> YCOCICCOH + OH     2.54E+35  -6.899  16223. ! mtbe017d.mec avg err
19.01%
C2C.COH + O2     <=> C2CQCO.            2.21E+29  -5.676  16481. ! mtbe017d.mec avg err
16.35%
```

```
C2C.COH + O2      <=> C2C.Q + HCHO       1.50E+51  -13.022   15334. ! mtbe017d.mec avg err
26.66%
C2C.COH + O2      <=> C2CQC.OH           1.69E+38   -8.202   14388. ! mtbe017d.mec avg err
19.02%
C2C.COH + O2      <=> C2C*COH + HO2      3.09E+37   -8.814    9776. ! mtbe017d.mec avg err
14.78%
C2CQ.COH          <=> C*CICCOHB + HO2B   4.95E+34   -6.838   13379. ! mtbe017d.mec avg err
18.42%
C2CQ.COH          <=> C2C*COHB + HO2B    2.17E+42   -9.219   42029. ! mtbe017d.mec avg err
20.59%
C2CQ.COH          <=> C2.CQCOH           5.23E+46  -10.512   37385. ! mtbe017d.mec avg err
14.17%
C2CQ.COH          <=> C*CICCOH + HO2     1.63E+65  -16.851   42253. ! mtbe017d.mec avg err
20.88%
C2CQ.COH          <=> YCOCICCOH + OH     9.42E+59  -14.507   47137. ! mtbe017d.mec avg err
24.01%
C2CQ.COH          <=> C2CQCO.            1.70E+52  -12.833   47258. ! mtbe017d.mec avg err 24.83%
C2CQ.COH          <=> C2C.Q + HCHO       7.80E+54  -14.278   31733. ! mtbe017d.mec avg err
64.73%
C2CQ.COH          <=> C2CQC.OH           2.59E+58  -14.427   42304. ! mtbe017d.mec avg err
18.09%
C2CQ.COH          <=> C2C*COH + HO2      1.85E+59  -15.352   35676. ! mtbe017d.mec avg err
16.88%
C2.CQCOH          <=> C*CICCOHB + HO2B   3.49E+56  -13.652   40737. ! mtbe017d.mec avg err
19.36%
C2.CQCOH          <=> C2C*COHB + HO2B    1.63E+33   -7.208   30034. ! mtbe017d.mec avg err
30.73%
C2.CQCOH          <=> C*CICCOH + HO2     2.27E+43  -10.157   29793. ! mtbe017d.mec avg err
24.45%
C2.CQCOH          <=> YCOCICCOH + OH     6.93E+32   -6.805   19638. ! mtbe017d.mec avg err
25.94%
C2.CQCOH          <=> C2CQCO.            2.77E+26   -5.440   21445. ! mtbe017d.mec avg err 28.98%
C2.CQCOH          <=> C2C.Q + HCHO       8.57E+66  -18.445   34615. ! mtbe017d.mec avg err
39.01%
C2.CQCOH          <=> C2CQC.OH           3.71E+54  -14.009   33794. ! mtbe017d.mec avg err
20.64%
C2.CQCOH          <=> C2C*COH + HO2      1.43E+57  -15.444   30469. ! mtbe017d.mec avg err
8.58%
C2CQCO.           <=> C*CICCOHB + HO2B   8.20E+52  -13.247   33213. ! mtbe017d.mec avg err
26.54%
C2CQCO.           <=> C2C*COHB + HO2B    2.27E+50  -12.203   30858. ! mtbe017d.mec avg err
21.25%
C2CQCO.           <=> C*CICCOH + HO2     1.06E+56  -13.852   27772. ! mtbe017d.mec avg err
38.32%
C2CQCO.           <=> YCOCICCOH + OH     8.73E+67  -17.490   36090. ! mtbe017d.mec avg err
35.70%
C2CQCO.           <=> C2C.Q + HCHO       9.47E+59  -15.749   35859. ! mtbe017d.mec avg err
28.33%
C2CQCO.           <=> C2CQC.OH           1.76E+30   -5.833   15527. ! mtbe017d.mec avg err  7.02%
C2CQCO.           <=> C2C*COH + HO2      3.89E+65  -17.863   25711. ! mtbe017d.mec avg err
40.36%
C2CQC.OH          <=> C*CICCOHB + HO2B   1.75E+65  -16.826   31012. ! mtbe017d.mec avg err
43.43%
```

```
C2CQC.OH        <=> C2C*COHB + HO2B     7.97E+30  -6.491  34647. ! mtbe017d.mec avg err
26.67%
C2CQC.OH        <=> C2C.Q + HCHO        2.80E+38  -8.707  32445. ! mtbe017d.mec avg err
17.49%
C2CQC.OH        <=> C2C*COH + HO2       1.44E+50 -12.691  36836. ! mtbe017d.mec avg err
14.03%
C2C*CQ          <=> C2C*CO. + OH        2.56E+32  -6.725  18456. ! mtbe017d.mec avg err 34.96%
C2.C*C + HO2     <=> C*CICCQ            3.85E+41  -9.419  24393. ! mtbe017d.mec avg err 49.14%
C2.C*C + HO2     <=> C*CICCO. + OH      2.59E+49 -11.759  10186. ! mtbe017d.mec avg err
24.51%
C*CICCQ         <=> C*CICCO. + OH       1.13E+21  -2.170   7943. ! mtbe017d.mec avg err
20.67%
C*CICCO.        <=> C*CICC*O + H        2.48E+48 -10.538  54973. ! mtbe017d.mec avg err
37.92%
C*CICCO.        <=> CC.*C + HCHO        9.65E+30  -6.461  16432. ! mtbe017d.mec avg err
27.97%
C2C.C*O + HO2    <=> C2CQC*O            8.28E+21  -3.687  23122. ! mtbe017d.mec avg err
23.58%
C2C.C*O + HO2    <=> C2C.Q + CHO        9.54E+45 -10.749   8788. ! mtbe017d.mec avg err
19.36%
C2C.C*O + HO2    <=> C2CQC.*O + H       1.16E+08   1.863  16906. ! mtbe017d.mec avg err
20.12%
C2C.C*O + HO2    <=> C2CO.C*O + OH      2.83E+07   1.323  31842. ! mtbe017d.mec avg err
104.85%
C2CQC*O         <=> C2C.Q + CHO         3.50E+22  -2.640   8138. ! mtbe017d.mec avg err 22.39%
C2CQC*O         <=> C2CQC.*O + H        8.13E+44  -9.294  79566. ! mtbe017d.mec avg err
22.87%
C2CQC*O         <=> C2CO.C*O + OH       4.00E+36  -7.735  91686. ! mtbe017d.mec avg err
25.56%
C2C.C*O + OH     <=> C2COHC*O           5.44E+44  -9.450  52149. ! mtbe017d.mec avg err
35.50%
C2C.C*O + OH     <=> C2C.OH + CHO       1.17E+57 -14.008  13588. ! mtbe017d.mec avg err
59.21%
C2C.C*O + OH     <=> C2COHC.*O + H      6.09E+19  -1.741   9443. ! mtbe017d.mec avg err
39.91%
C2COHC*O        <=> C2C.OH + CHO        6.26E+08   .417   12653. ! mtbe017d.mec avg err
24.31%
C2COHC*O        <=> C2COHC.*O + H       7.04E+52 -11.090  84381. ! mtbe017d.mec avg err
71.42%
C2COHC.*O       <=> C2C.OH + CO         2.16E+60 -14.468 101643. ! mtbe017d.mec avg err
47.26%
C2CQC.*O        <=> C2C.Q + CO          4.61E+12  -1.182   2311. ! mtbe017d.mec avg err 22.23%
YCOCICCQ         <=> CCYC.OC + CH2OOH   3.99E+11   -.803   2247. ! mtbe017d.mec avg err
16.82%
YCOCICCQ         <=> YCOCICCO. + OH     1.65E+40  -8.278  90863. ! mtbe017d.mec avg err
31.78%
YCOCICCOH        <=> CCYC.OC + CH2OH    2.28E+48 -10.498  54373. ! mtbe017d.mec avg err
36.97%
C2C.Q           <=> C2C*O + OH          2.32E+36  -6.131  89864. ! mtbe017d.mec avg err 60.79%
CCYC.OC          <=> C2.C*O             3.05E+09   -.134   -376. ! mtbe017d.mec avg err  2.12%
C2CYCOC          <=> CCYC.OC + CH3      1.18E+12   -.994   1702. ! mtbe017d.mec avg err
8.18%
C2C*O           <=> CH3C.*O + CH3       4.81E+40  -7.326  93465. ! mtbe017d.mec avg err 70.70%
```

```
C*CICC*O        <=> CC.*C + CHO       5.09E+47  -9.779  90106. ! mtbe017d.mec avg err
38.51%
C*CICC*O        <=> C*CICC.*O + H     3.88E+36  -6.109  102355. ! mtbe017d.mec avg err
53.96%
C*CICC.*O       <=> CC.*C + CO        1.33E+25  -3.336  85773. ! mtbe017d.mec avg err 39.34%
C2.C*O          <=> C*C*O + CH3       2.49E+44  -9.813  41318. ! mtbe017d.mec avg err 19.74%
C2CYCOC.        <=> C2C.C*O           6.12E+30  -5.755  42358. ! mtbe017d.mec avg err 26.21%
C2CYCOC.        <=> C*CICC*O + H      3.11E+37  -9.012  10250. ! mtbe017d.mec avg err
12.52%
C2CYCOC.        <=> C2C*C*O + H       9.07E+12  -1.067  12137 ! mtbe017d.mec avg err
37.62%
C2CYCOC.        <=> C2CC.*O           5.70E+12  -1.051  12342. ! mtbe017d.mec avg err 37.20%
C2CYCOC.        <=> CC.C + CO         2.85E+06  -.359   6461. ! mtbe017d.mec avg err 24.55%
C2C.C*O         <=> C*CICC*O + H      3.75E+11  -.573   10111. ! mtbe017d.mec avg err 40.72%
C2C.C*O         <=> C2C*C*O + H       3.14E+40  -8.636  47876. ! mtbe017d.mec avg err 27.00%
C2C.C*O         <=> C2CC.*O           3.29E+40  -8.686  48278. ! mtbe017d.mec avg err 26.31%
C2C.C*O         <=> CC.C + CO         3.95E+28  -6.278  37898. ! mtbe017d.mec avg err 15.97%
C2CC.*O         <=> CC.C + CO         1.36E+34  -6.684  41715. ! mtbe017d.mec avg err 32.78%
C2C.C*O + O2    <=> C2CQ.C*O          4.15E+21  -3.789  9000. ! mtbe017d.mec avg err 35.30%
C2C.C*O + O2    <=> C2CQC.*O          1.13E+29  -5.953  2554. ! mtbe017d.mec avg err 16.53%
C2C.C*O + O2    <=> C2C.Q + CO        4.45E+19  -3.548  4470. ! mtbe017d.mec avg err  5.57%
C2C.C*O + O2    <=> C2C*C*O + HO2     2.72E+23  -3.346  6161. ! mtbe017d.mec avg err
6.68%
C2C.C*O + O2    <=> C2.CQC*O          3.92E+08   .429   6318. ! mtbe017d.mec avg err  3.05%
C2C.C*O + O2    <=> C*CQC + CHO       7.11E+11  -.878   6977. ! mtbe017d.mec avg err
5.62%
C2C.C*O + O2    <=> C*CICC*O + HO2    1.28E+05  2.056  17110. ! mtbe017d.mec avg err
4.08%
C2CQ.C*O        <=> C2CQC.*O          2.19E+14  -.674  10322. ! mtbe017d.mec avg err  1.30%
C2CQ.C*O        <=> C2C.Q + CO        3.11E+31  -7.778  17941. ! mtbe017d.mec avg err  2.99%
C2CQ.C*O        <=> C2C*C*O + HO2     2.72E+33  -7.062  19407. ! mtbe017d.mec avg err
11.52%
C2CQ.C*O        <=> C2.CQC*O          1.75E+17  -2.877  22496. ! mtbe017d.mec avg err 16.70%
C2CQ.C*O        <=> C*CQC + CHO       2.42E+25  -5.489  27214. ! mtbe017d.mec avg err
17.24%
C2CQ.C*O        <=> C*CICC*O + HO2    3.44E+11  -.549   36566. ! mtbe017d.mec avg err
18.69%
C2CQC.*O        <=> C2C*C*O + HO2     2.92E+25  -4.628  29752. ! mtbe017d.mec avg err
20.98%
C2CQC.*O        <=> C2.CQC*O          4.20E+08  -.155   16190. ! mtbe017d.mec avg err  5.80%
C2CQC.*O        <=> C*CQC + CHO       1.28E-12  3.881  -7080. ! mtbe017d.mec avg err
38.18%
C2CQC.*O        <=> C*CICC*O + HO2    5.95E+05   .566  36445. ! mtbe017d.mec avg err
5.13%
C2.CQC*O        <=> C2C.Q + CO        4.81E-08  3.938  8569. ! mtbe017d.mec avg err 53.88%
C2.CQC*O        <=> C2C*C*O + HO2     3.09E-03  2.630  -4224. ! mtbe017d.mec avg err
69.20%
C2.CQC*O        <=> C*CQC + CHO       6.10E-29  9.765  -5291. ! mtbe017d.mec avg err
43.81%
C2.CQC*O        <=> C*CICC*O + HO2    1.07E+11  -.348  21393. ! mtbe017d.mec avg err
8.74%
C2.C*O + HCHO   <=> CHO + C2C*O       6.30E+07  1.90   18191. ! 1/2
C2.C*O + C2C*C  <=> C2C*O + C2.C*C    1.01E-01  4.00   227. !
C2.C*O + C3COC  <=> C2C*O + C3COC.    1.78E+02  3.30   19844. !1/2 (c
```

```
C2.C*O + C3COC      <=> C2C*O + C3.COC      8.70E+02   2.90   19314. !1/2 (c
C2.C*O + CH3OH      <=> C2C*O + CH2OH       8.70E+02   2.90   20456. !1/2 (c
C2.C*O + C2CYCOC    <=> C2C*O + C2CYCOC.    5.00E-01   4.00   13318. !1/2 (c
C2.C*O + CCYCOC     <=> C2C*O + CCYC.OC     2.21E-01   3.30   17169. !1/2 (c
C2.C*O + C*CICC*O   <=> C2C*O + C*CICC.*O   1.25E+07   0.00       0. !1/2 (c
C2.C*O + C2CC*O     <=> C2C*O + C2CC.*O     2.51E+07   0.00       0. !the sa
C2.C*O + O*CC*O     <=> C2C*O + O*CC.*O     5.02E+07   0.00       0. !2*ch3c
C2.C*O + CCC*O      <=> C2C*O + CCC.*O      2.51E+07   0.00       0. !the sa
C2.C*O + CH3CHO     <=> C2C*O + CH3C.*O     2.51E+07   0.00       0. !70 SCH
C2.C*O + C2CQC*O    <=> C2C*O + C2CQC.*O    1.25E+07   0.00       0. !1/2 (c
C2.C*O + C2COHC*O   <=> C2C*O + C2COHC.*O   1.25E+07   0.00       0. !1/2 (c
C2.C*O + CCQCHO     <=> C2C*O + CCQC.*O     1.25E+07   0.00       0. !1/2 (c
C2.C*O + CCOHCHO    <=> C2C*O + CCOHC.*O    1.25E+07   0.00       0. !1/2 (c
C2C*O + O         <=> C2.C*O + OH         2.28E+12   0.00    4961. !88HER
C2C*O + H         <=> C2.C*O + H2         1.86E+13   0.00    6357. !76AMB
C2C*O + OH        <=> C2.C*O + H2O        1.02E+12   0.00    1192. !92&89
C2C*O + CH3       <=> C2.C*O + CH4        3.29E+11   0.00    9600. !nist
C2C*O + CH3O      <=> C2.C*O + CH3OH      3.29E+11   0.00    9600. !take
C2C*O + HO2       <=> C2.C*O + H2O2       3.29E+11   0.00    9600. !nist
C2C*O + O2        <=> C2.C*O + HO2        3.29E+11   0.00    9600. !nist
C2CYCOC + OH      <=>  C2CYCOC. + H2O     1.55E+06   2.0    -1458.  ! 84
C2CYCOC+CH3OO     <=> C2CYCOC.+CH3OOH     1.00E+00   4.0    13318.  ! !
C2CYCOC + O       <=> C2CYCOC. + OH       4.00E+07   0.0        0. ! 88 H
C2CYCOC + H       <=>  C2CYCOC. + H2      8.00E+13   0.0     9680. ! 84 B
C2CYCOC + CH3     <=> C2CYCOC. + CH4      1.02E-01   4.0     4915. ! AMDC
C2CYCOC + CH3O    <=> C2CYCOC. + CH3OH    1.02E-01   4.0     4915. ! AMDC
C2CYCOC + HO2     <=> C2CYCOC. + H2O2     1.00E+00   4.0    13318.   !
CCYCOC + O        <=> CCYC.OC + OH        1.56E+05   2.50    1113. ! 90 T
CCYCOC + H        <=> CCYC.OC + H2        6.02E+05   2.40    2583. ! 90 T
CCYCOC + OH       <=> CCYC.OC + H2O       5.73E+10   0.51      64. ! 90 T
CCYCOC + CH3      <=> CCYC.OC + CH4       9.04E-01   3.46    4598. ! 90 T
CCYCOC + CH3O     <=> CCYC.OC + CH3OH     2.29E+10   0.00    2873. ! 90 T
CCYCOC + CH3OO    <=> CCYC.OC + CH3OOH    3.61E+03   2.55   10532. ! 90 T
CCYCOC + HO2      <=> CCYC.OC + H2O2      3.61E+03   2.55   10532. ! 90 T
CCYCOC + CH2OH    <=> CCYC.OC + CH3OH     1.21E+02   2.76   10796. ! 90 T
CCYCOC + O2       <=> CCYC.OC + HO2       3.97E+13   0.00   43997. ! 90 T
C*CICC*O + O      <=> C*CICC.*O + OH      1.40E+13   0.00    2401. !75 GAF
C*CICC*O + H      <=> C*CICC.*O + H2      8.09E+11   0.00       0. !78 KOD
C*CICC*O + OH     <=> C*CICC.*O + H2O     1.60E+13   0.00       0. !80 MAL
C*CICC*O + CH3    <=> C*CICC.*O + CH4     4.25E+10   0.00    4999. !A/2.E-
C*CICC*O + CH3O   <=> C*CICC.*O + CH3OH   4.25E+10   0.00    4999. !A/2.E-
C*CICC*O + O2     <=> C*CICC.*O + HO2     1.50E+13   0.00   38148. !A/2.E-
C*CICC*O + HO2    <=> C*CICC.*O + H2O2    1.50E+12   0.00   10923. !A/2.E-
C2CC*O + O        <=> C2CC.*O + OH        5.00E+12   0.00    1792. !84 WAR
C2CC*O + H        <=> C2CC.*O + H2        4.00E+13   0.00    4207. !84 WAR
C2CC*O + OH       <=> C2CC.*O + H2O       1.00E+13   0.00       0. !84 WAR
C2CC*O + CH3      <=> C2CC.*O + CH4       8.49E+10   0.00    5999. !84 WAR
C2CC*O + CH3O     <=> C2CC.*O + CH3OH     8.49E+10   0.00    5999. !84 WAR
C2CC*O + O2       <=> C2CC.*O + HO2       3.01E+13   0.00   39148. !92BAU/
C2CC*O + HO2      <=> C2CC.*O + H2O2      3.01E+12   0.00   11923. !92BAU/
O*CC*O + O        <=> O*CC.*O + OH        3.01E+08   0.00       0. !85 NIK
O*CC*O + H        <=> O*CC.*O + H2        8.00E+13   0.00    4207. ! 2* 84
O*CC*O + OH       <=> O*CC.*O + H2O       6.62E+12   0.00       0. !92 BAU
O*CC*O + CH3      <=> O*CC.*O + CH4       1.70E+11   0.00    5999. ! 2* 84
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O*CC*O + CH3O      <=> O*CC.*O + CH3OH     1.70E+11   0.00    5999. ! 2* 84
O*CC*O + O2        <=> O*CC.*O + HO2       6.02E+13   0.00   39148. ! 2* 92
O*CC*O + HO2       <=> O*CC.*O + H2O2      6.02E+12   0.00   11923. ! 2* 92
CCC*O + O          <=> CCC.*O + OH         5.68E+12   0.00    1542. !77 SIN
CCC*O + H          <=> CCC.*O + H2         4.00E+13   0.00    4207. !84 WAR
CCC*O + OH         <=> CCC.*O + H2O        1.00E+13   0.00       0 !84 WAR
CCC*O + CH3        <=> CCC.*O + CH4        8.49E+10   0.00    5999. !84 WAR
CCC*O + CH3O       <=> CCC.*O + CH3OH      8.49E+10   0.00    5999. !84 WAR
CCC*O + O2         <=> CCC.*O + HO2        3.01E+13   0.00   39148. !92BAU/
CCC*O + HO2        <=> CCC.*O + H2O2       3.01E+12   0.00   11923. !92BAU/
CH3CHO + O         <=> CH3C.*O + OH        5.00E+12   0.00    1792. !84 WAR
CH3CHO + H         <=> CH3C.*O + H2        4.00E+13   0.00    4207. !84 WAR
CH3CHO + OH        <=> CH3C.*O + H2O       4.16E+11   0.57    2762. !92BAU/
CH3CHO + CH3       <=> CH3C.*O + CH4       8.49E+10   0.00    5999. !84 WAR
CH3CHO + CH3O      <=> CH3C.*O + CH3OH     8.49E+10   0.00    5999. !84 WAR
CH3CHO + O2        <=> CH3C.*O + HO2       3.01E+13   0.00   39148. !92BAU/
CH3CHO + HO2       <=> CH3C.*O + H2O2      3.01E+12   0.00   11923. !92BAU/
C2CQC*O + O        <=> C2CQC.*O + OH       2.50E+12   0.00    1792. !1/2 84
C2CQC*O + H        <=> C2CQC.*O + H2       2.00E+13   0.00    4207. !1/2 84
C2CQC*O + OH       <=> C2CQC.*O + H2O      2.08E+11   0.57    2762. !1/2 92
C2CQC*O + CH3      <=> C2CQC.*O + CH4      4.25E+10   0.00    5999. !1/2 84
C2CQC*O + CH3O     <=> C2CQC.*O + CH3OH    4.25E+10   0.00    5999. !1/2 84
C2CQC*O + O2       <=> C2CQC.*O + HO2      1.50E+13   0.00   39148. !1/2 92
C2CQC*O + HO2      <=> C2CQC.*O + H2O2     1.50E+12   0.00   11923. !1/2 92
C2COHC*O + O       <=> C2COHC.*O + OH      2.50E+12   0.00    1792. !1/2 84
C2COHC*O + H       <=> C2COHC.*O + H2      2.00E+13   0.00    4207. !1/2 84
C2COHC*O + OH      <=> C2COHC.*O + H2O     2.08E+11   0.57    2762. !1/2 92
C2COHC*O + CH3     <=> C2COHC.*O + CH4     4.25E+10   0.00    5999. !1/2 84
C2COHC*O + CH3O    <=> C2COHC.*O + CH3OH   4.25E+10   0.00    5999. !1/2 84
C2COHC*O + O2      <=> C2COHC.*O + HO2     1.50E+13   0.00   39148. !1/2 92
C2COHC*O + HO2     <=> C2COHC.*O + H2O2    1.50E+12   0.00   11923. !1/2 92
CCQCHO + O         <=> CCQC.*O + OH        2.50E+12   0.00    1792. !1/2 84
CCQCHO + H         <=> CCQC.*O + H2        2.00E+13   0.00    4207. !1/2 84
CCQCHO + OH        <=> CCQC.*O + H2O       2.08E+11   0.57    2762. !1/2 92
CCQCHO + CH3       <=> CCQC.*O + CH4       4.25E+10   0.00    5999. !1/2 84
CCQCHO + CH3O      <=> CCQC.*O + CH3OH     4.25E+10   0.00    5999. !1/2 84
CCQCHO + O2        <=> CCQC.*O + HO2       1.50E+13   0.00   39148. !1/2 92
CCQCHO + HO2       <=> CCQC.*O + H2O2      1.50E+12   0.00   11923. !1/2 92
CCOHCHO + O        <=> CCOHC.*O + OH       2.50E+12   0.00    1792. !1/2 84
CCOHCHO + H        <=> CCOHC.*O + H2       2.00E+13   0.00    4207. !1/2 84
CCOHCHO + OH       <=> CCOHC.*O + H2O      2.08E+11   0.57    2762. !1/2 92
CCOHCHO + CH3      <=> CCOHC.*O + CH4      4.25E+10   0.00    5999. !1/2 84
CCOHCHO + CH3O     <=> CCOHC.*O + CH3OH    4.25E+10   0.00    5999. !1/2 84
CCOHCHO + O2       <=> CCOHC.*O + HO2      1.50E+13   0.00   39148. !1/2 92
CCOHCHO + HO2      <=> CCOHC.*O + H2O2     1.50E+12   0.00   11923. !1/2 92
C*CC*O + O         <=> C*CC.*O + OH        1.40E+13   0.00    2401. !75 GAF
C*CC*O + H         <=> C*CC.*O + H2        8.09E+11   0.00       0. !78 KOD
C*CC*O + OH        <=> C*CC.*O + H2O       1.60E+13   0.00       0. !80 MAL
C*CC*O + CH3       <=> C*CC.*O + CH4       4.25E+10   0.00    4999. !A/2.E-
C*CC*O + CH3O      <=> C*CC.*O + CH3OH     4.25E+10   0.00    4999. !A/2.E-
C*CC*O + O2        <=> C*CC.*O + HO2       1.50E+13   0.00   38148. !A/2.E-
C*CC*O + HO2       <=> C*CC.*O + H2O2      1.50E+12   0.00   10923. !A/2.E-
C2.C*C + C2C*C     <=> C2C*C + C2.C*C      2.23E+01   3.50    6637. ! RXN6
C2.C*C + C3COC     <=> C2C*C + C3.COC      3.56E+02   3.30   19844. !data f
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C2.C*C + C3COC     <=> C2C*C + C3COC.     1.74E+03   2.90   19314. !data f
C2.C*C + CH3OH     <=> C2C*C + CH2OH      1.74E+03   2.90   20456. !data f
C2.C*C + HCHO      <=> CHO + C2C*C        1.26E+08   1.90   18191. !86TSA/
C2.C*C + C2CYCOC   <=> C2C*C + C2CYCOC.   1.00E+00   4.00   13318. !AMD CH
C2.C*C + CCYCOC    <=> C2C*C + CCYC.OC    4.22E+01   3.30   17169. !data f
C2.C*C + C*CICC*O  <=> C2C*C + C*CICC.*O  1.90E+11   0.00   6218. !data f
C2.C*C + C2CC*O    <=> C2C*C + C2CC.*O    3.80E+11   0.00   7218. !data f
C2.C*C + O*CC*O    <=> C2C*C + O*CC.*O    7.90E+11   0.00   7218. !data f
C2.C*C + CCC*O     <=> C2C*C + CCC.*O     3.80E+11   0.00   7218. !data f
C2.C*C + CH3CHO    <=> C2C*C + CH3C.*O    3.80E+11   0.00   7218. !data f
C2.C*C + C2CQC*O   <=> C2C*C + C2CQC.*O   1.90E+11   0.00   7218. !data f
C2.C*C + C2COHC*O  <=> C2C*C + C2COHC.*O  1.90E+11   0.00   7218. !data f
C2.C*C + CCQCHO    <=> C2C*C + CCQC.*O    1.90E+11   0.00   7218. !data f
C2.C*C + CCOHCHO   <=> C2C*C + CCOHC.*O   1.90E+11   0.00   7218. !data f
C2.C*C          <=> C*C*C + CH3        2.25E+15  -1.870   4734. ! mtbe017d.mec avg err 16.07%
C2.C*C + O2     <=> C*CICCQ.           5.30E+24  -3.637  55355. ! mtbe017d.mec avg err 29.88%
C2.C*C + O2     <=> C*CICCO. + O       6.80E+28  -5.919   3261. ! mtbe017d.mec avg err
15.76%
C2.C*C + O2     <=> C*CICC.Q           3.17E+16  -1.051  42827. ! mtbe017d.mec avg err  3.03%
C2.C*C + O2     <=> C*CICC*O + OH      9.83E+06   .337   20445. ! mtbe017d.mec avg err
6.64%
C2.C*C + O2     <=> C*CIC.CQ           2.17E+11   .499   21331. ! mtbe017d.mec avg err  2.57%
C2.C*C + O2     <=> C*C*C + CH2OOH     6.74E+31  -6.172   9528. ! mtbe017d.mec avg err
4.97%
C2.C*C + O2     <=> C*CYCCOC + OH      1.91E+15  -.446   41097. ! mtbe017d.mec avg err
8.96%
C2.C*C + O2     <=> CCYC.COOC          2.35E+19  -2.109   17979. ! mtbe017d.mec avg err
9.12%
C2.C*C + O2     <=> C2.CYCOOC          1.83E+29  -6.422   18935. ! mtbe017d.mec avg err
17.69%
C2.C*C + O2     <=> CCYCC.OOC          3.86E+10  -.793   16420. ! mtbe017d.mec avg err
5.76%
C2.C*C + O2     <=> YCOCICCO.          3.45E+04   .749   24249. ! mtbe017d.mec avg err 16.77%
C2.C*C + O2     <=> CCYC.OC+HCHO       2.13E+08  -.585   13591. ! mtbe017d.mec avg err
17.57%
C2.C*C + O2     <=> C2CYCOOC.          2.10E+12  -.313   17050. ! mtbe017d.mec avg err  3.20%
C2.C*C + O2     <=> CCICO.C*O          1.05E-06   3.629   31834. ! mtbe017d.mec avg err  8.07%
C2.C*C + O2     <=> CC.C*O + HCHO      3.07E-02   2.780   20289. ! mtbe017d.mec avg err
11.71%
C2.C*C + O2     <=> C2CO.C*O           8.88E+05   1.598   24012. ! mtbe017d.mec avg err 14.55%
C2.C*C + O2     <=> C2C*O + CHO        1.30E-05   3.424   32184. ! mtbe017d.mec avg err  6.87%
C*CICCQ.        <=> C*CICCO. + O       2.16E-04   4.236   32097. ! mtbe017d.mec avg err  8.10%
C*CICCQ.        <=> C*CICC.Q           5.26E+15  -1.531   58012. ! mtbe017d.mec avg err 16.37%
C*CICCQ.        <=> C*CICC*O + OH      2.95E+11  -1.638   36430. ! mtbe017d.mec avg err
15.33%
C*CICCQ.        <=> C*CIC.CQ           5.49E+15  -1.462   37266. ! mtbe017d.mec avg err 19.12%
C*CICCQ.        <=> C*C*C + CH2OOH     4.31E+41  -9.638   22293. ! mtbe017d.mec avg err
7.14%
C*CICCQ.        <=> C*CYCCOC + OH      2.77E+15  -1.196   56577. ! mtbe017d.mec avg err
11.59%
C*CICCQ.        <=> CCYC.COOC          4.04E+25  -4.600   33463. ! mtbe017d.mec avg err
12.38%
C*CICCQ.        <=> C2.CYCOOC          1.99E+35  -8.720   35245. ! mtbe017d.mec avg err
32.93%
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C*CICCQ.        <=> CCYCC.OOC          3.31E+16  -3.186  32364. ! mtbe017d.mec avg err
15.74%
C*CICCQ.        <=> YCOCICCO.          5.68E+06   -.588  39292. ! mtbe017d.mec avg err  8.51%
C*CICCQ.        <=> CCYC.OC+HCHO       1.52E+14  -2.928  29598. ! mtbe017d.mec avg err
44.20%
C*CICCQ.        <=> C2CYCOOC.          1.02E+18  -2.642  32881. ! mtbe017d.mec avg err
18.90%
C*CICCQ         <=> CCICO.C*O          3.88E-06   2.738  47078. ! mtbe017d.mec avg err 15.00%
C*CICCQ.        <=> CC.C*O + HCHO      4.69E+00   1.459  35334. ! mtbe017d.mec avg err
20.41%
C*CICCQ.        <=> C2CO.C*O           1.24E+08    .279  39014. ! mtbe017d.mec avg err 10.37%
C*CICCQ.        <=> C2C*O + CHO        5.16E-05   2.525  47447. ! mtbe017d.mec avg err 16.55%
C*CICC.Q        <=> C*CICC*O + OH      8.54E-04   3.337  47357. ! mtbe017d.mec avg err
15.05%
C*CICC.Q        <=> C*CIC.CQ           7.41E+08    .034   -607. ! mtbe017d.mec avg err  3.53%
C*CICC.Q        <=> CCYC.COOC          2.61E-01    .639  -4359. ! mtbe017d.mec avg err 28.62%
C*CICC.Q        <=> C2.CYCOOC          5.58E+13  -4.567    673. ! mtbe017d.mec avg err  9.04%
C*CIC.CQ        <=> C*C*C + CH2OOH     2.96E+19  -5.908   4510. ! mtbe017d.mec avg err
31.41%
C*CIC.CQ        <=> C*CYCCOC + OH      1.29E+15  -1.040  53521. ! mtbe017d.mec avg err
10.50%
C*CIC.CQ        <=> CCYC.COOC          6.26E+19  -2.895  28050. ! mtbe017d.mec avg err  5.71%
C*CIC.CQ        <=> C2.CYCOOC          1.59E+38  -9.520  36350. ! mtbe017d.mec avg err
27.28%
CCYC.COOC       <=> C2.CYCOOC          9.90E+18  -3.826  33336. ! mtbe017d.mec avg err
9.67%
CCYC.COOC       <=> YCOCICCO.          2.80E-14   4.504   8165. ! mtbe017d.mec avg err
134.24%
CCYC.COOC       <=> CCYC.OC+HCHO       3.10E+35  -8.775  25698. ! mtbe017d.mec avg err
15.66%
CCYC.COOC       <=> CCYCC.OOC          2.86E+38  -8.300  28883. ! mtbe017d.mec avg err
9.28%
CCYC.COOC       <=> CCICO.C*O          1.11E-18   6.935  13494. ! mtbe017d.mec avg err
68.28%
CCYC.COOC       <=> CC.C*O + HCHO      3.82E-11   5.151  19149. ! mtbe017d.mec avg err
81.23%
C2.CYCOOC       <=> YCOCICCO.          4.01E-03   3.796  23289. ! mtbe017d.mec avg err
97.99%
C2.CYCOOC       <=> CCYC.OC+HCHO       2.34E+10  -1.812  -2283. ! mtbe017d.mec avg err
21.81%
C2.CYCOOC       <=> C2CYCOOC.          2.07E+11   -.660    608. ! mtbe017d.mec avg err  2.02%
C2.CYCOOC       <=> C2CO.C*O           1.07E-67  20.391 -18520. ! mtbe017d.mec avg err
78.76%
C2.CYCOOC       <=> C2C*O + CHO        1.52E-71  21.784 -17283. ! mtbe017d.mec avg err
109.40%
CCYCC.OOC       <=> CCICO.C*O          2.41E-70  22.604 -17332. ! mtbe017d.mec avg err
111.64%
CCYCC.OOC       <=> CC.C*O + HCHO      3.47E+07   -.465  -2618. ! mtbe017d.mec avg err
9.76%
YCOCICCO.       <=> CCYC.OC+HCHO       2.69E+12   -.915    630. ! mtbe017d.mec avg err
1.10%
C2CYCOOC.       <=> C2CO.C*O           8.98E+30  -6.438  15815. ! mtbe017d.mec avg err
44.34%
```

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C2CYCOOC.       <=> C2C*O + CHO       5.58E+09  -1.311   -272. ! mtbe017d.mec avg err
.27%
CCICO.C*O       <=> CC.C*O + HCHO     6.55E+10  - 457   -385. ! mtbe017d.mec avg err
1.41%
C2CO.C*O        <=> C2C*O + CHO       6.47E+18  -2.948   6595. ! mtbe017d.mec avg err
22.35%
CC C*O        <=> C*CC*O + H        1.74E+12   -.882    152. ! mtbe017d.mec avg err  4.88%
CC.C*O        <=> CC*C*O + H        3.99E+40  -8.736  45673. ! mtbe017d.mec avg err 17.53%
CC.C*O        <=> CCC.*O          2.00E+30  -6.266  32648. ! mtbe017d.mec avg err 31.72%
CC.C*O        <=> C2H5 + CO         5.27E+32  -7.546  38484. ! mtbe017d.mec avg err  7.22%
CCC.*O        <=> C2H5 + CO         1.25E+35  -7.052  41157. ! mtbe017d.mec avg err 25.02%
CH3OH + O       <=> CH2OH + OH        1.72E+13   0.00   4914. !NIST F
CH3OH + O       <=> CH3O + OH         1.00E+13   0.00   5129. !A from
CH3OH + H       <=> CH2OH + H2        3.40E+13   0.00   5497. !A from
CH3OH + H       <=> CH3O + H2         4.00E+13   0.00   6095. !84 WAR
CH3OH + OH       <=> CH2OH + H2O       1.35E+13   0.00   1881. !NIST F
CH3OH + OH       <=> CH3O + H2O        1.00E+13   0.00   1953. !A from
CH3OH + CH3      <=> CH2OH + CH4       3.19E+01   3.20   7172. !87 TSA
CH3OH + CH3      <=> CH3O + CH4        1.44E+01   3.10   6935. !87 TSA
CH3OH + CH3O      <=> CH2OH + CH3OH     3.01E+11   0.00   4074. !87 TSA
CH3OH + HO2      <=> CH2OH + H2O2      9.64E+10   0.00  12579. !87 TSA
CH3OH + O2       <=> CH2OH + HO2       2.05E+13   0.00  44911. !87 TSA
CH3 + OH        <=> CH3OH           2.84E+27  -5.499  13233. ! mtbe017d.mec avg err 25.65%
CH3 + OH        <=> CH2S + H2O        1.67E+34  -6.747   5582. ! mtbe017d.mec avg err 18.78%
CH3 + OH        <=> HCOH + H2         2.77E+14   -.508   2729. ! mtbe017d.mec avg err  5.94%
CH3 + OH        <=> HCHO + H2         2.04E+16  -1.146   2772. ! mtbe017d.mec avg err  6.51%
CH3 + OH        <=> CH2OH + H         1.94E+08   1.030   3927. ! mtbe017d.mec avg err  3.86%
CH3 + OH        <=> CH3O + H          1.95E+13   -.087   6228. ! mtbe017d.mec avg err  2.54%
CH3OH         <=> CH2S + H2O        8.91E+12   -.302  13599. ! mtbe017d.mec avg err  .34%
CH3OH         <=> HCOH + H2         1.46E+36  -6.939  96720. ! mtbe017d.mec avg err 22.15%
CH3OH         <=> HCHO + H2         5.63E+32  -5.899  93292. ! mtbe017d.mec avg err 24.60%
CH3OH         <=> CH2OH + H         1.12E+31  -5.813  99212. ! mtbe017d.mec avg err 18.04%
CH3OH         <=> CH3O + H          1.53E+36  -7.048 102724. ! mtbe017d.mec avg err 15.67%
CH3 + O         <=> CH3O            4.64E+32  -6.514 108860. ! mtbe017d.mec avg err 12.95%
CH3 + O         <=> HCHO + H          7.24E+19  -3.378    758. ! mtbe017d.mec avg err  4.90%
CH3 + O         <=> CH2OH           5.65E+13   -.052   -253. ! mtbe017d.mec avg err  1.95%
CH3O          <=> HCHO + H          1.12E+24  -1.167   2710. ! mtbe017d.mec avg err  5.83%
CH3O          <=> CH2OH           9.20E+29  -6.055  27052. ! mtbe017d.mec avg err  5.24%
CH2OH         <=> HCHO + H          1.57E+38  -9.055  44503. ! mtbe017d.mec avg err 12.57%
CH2OH + O2      <=> CQ.H2OH           2.22E+30  -5.916  40127. ! mtbe017d.mec avg err 14.62%
CH2OH + O2      <=> HOCH2O. + O       3.40E+41  -9.552   7060. ! mtbe017d.mec avg err
9.42%
CH2OH + O2      <=> CQH2O.            2.99E+13   -.294  25339. ! mtbe017d.mec avg err 18.67%
CH2OH + O2      <=> HCHO + HO2        6.13E+14  -2.035   2213. ! mtbe017d.mec avg err
1.32%
CH2OH + O2      <=> HOC.HQ            1.76E+18  -1.965   4070. ! mtbe017d.mec avg err  3.86%
CH2OH + O2      <=> HCO2H + OH        5.31E+09   -.515   6821. ! mtbe017d.mec avg err  2.08%
CH2OH + O2      <=> HCQ*O + H         7.57E+10   .390   6433. ! mtbe017d.mec avg err  .81%
CQ.H2OH       <=> HOCH2O. + O       1.38E-01   3.327   4843. ! mtbe017d.mec avg err  .87%
CQ.H2OH       <=> CQH2O.            2.54E+25  -4.828  61426. ! mtbe017d.mec avg err 20.77%
CQ*H2OH       <=> HCHO + HO2        6.55E+31  -7.403  35589. ! mtbe017d.mec avg err 21.97%
CQ.H2OH       <=> HOC.HQ            5.90E+37  -8.168  38393. ! mtbe017d.mec avg err 24.47%
CQ.H2OH       <=> HCO2H + OH        1.96E+32  -7.955  45255. ! mtbe017d.mec avg err  9.09%
CQ.H2OH       <=> HCQ*O + H         3.37E+33  -7.080  44878. ! mtbe017d.mec avg err  7.79%
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CQH2O.          <=> HCHO + HO2       2.59E+22  -4.475  43083. ! mtbe017d.mec avg err  9.27%
CQH2O.          <=> HOC.HQ           2.64E+13  -1.392   2869. ! mtbe017d.mec avg err  8.86%
CQH2O.          <=> HCO2H + OH       1.42E+18  -4.679   5443. ! mtbe017d.mec avg err  4.37%
HOC.HQ          <=> HCO2H + OH       1.08E+19  -3.706   5015. ! mtbe017d.mec avg err  3.46%
HOC.HQ          <=> HCQ*O + H        2.79E+12  -.931     713. ! mtbe017d.mec avg err  1.06%
CHO + O2        <=> HCQ *O           1.13E+12  -.920   21519. ! mtbe017d.mec avg err  1.81%
CHO + O2        <=> HCO2. + O        1.34E+35  -7.676   4877. ! mtbe017d.mec avg err  5.72%
CHO + O2        <=> C.Q*O            1.54E+15  -.591   11927. ! mtbe017d.mec avg err  4.75%
CHO + O2        <=> CO + HO2         2.79E+15  -1.459   2078. ! mtbe017d.mec avg err  3.40%
CHO + O2        <=> CO2 + OH         7.32E+13  -.543    2007. ! mtbe017d.mec avg err  1.06%
HCQ.*O          <=> HCO2. + O        3.62E+16  -1.172   2432. ! mtbe017d.mec avg err  1.85%
HCQ.*O          <=> C.Q*O            2.80E+31  -6.300  55096. ! mtbe017d.mec avg err  3.53%
HCQ *O          <=> CO + HO2         2.12E+35  -7.913  41535. ! mtbe017d.mec avg err 15.50%
HCQ.*O          <=> CO2 + OH         4.73E+34  -7.358  41727. ! mtbe017d.mec avg err 12.45%
C.Q*O           <=> CO + HO2         3.44E+36  -7.663  41916. ! mtbe017d.mec avg err 13.72%
C.Q*O           <=> CO2 + OH         5.08E+11  -.735   12689. ! mtbe017d.mec avg err  1.23%
HCQ*O           <=> HCO2. + OH       4.74E+12  -1.026   1578. ! mtbe017d.mec avg err   .59%
HCO2.           <=> CO2 + H          5.13E+43  -9.732  42403. ! mtbe017d.mec avg err  6.69%
HCO2.           <=> C.O2H            2.27E+30  -6.086  37422. ! mtbe017d.mec avg err  6.18%
HCO2.           <=> CO + OH          6.48E+35  -8.598  41151. ! mtbe017d.mec avg err  5.56%
C.O2H           <=> CO2 + H          5.09E+29  -5.899  40723. ! mtbe017d.mec avg err  8.48%
C.O2H           <=> CO + OH          1.45E+25  -4.994  34719. ! mtbe017d.mec avg err  6.27%
HCO2H           <=> CO + H2O         1.13E+26  -5.016  21027. ! mtbe017d.mec avg err  3.64%
HCO2H           <=> CO2 + H2         7.57E+25  -4.224  65105. ! mtbe017d.mec avg err 17.88%
HCHO + O        <=> CHO + OH         4.16E+11   0.57    2762. !92BAU/
HCHO + H        <=> CHO + H2         2.29E+10   1.05    3279. !92BAU/
HCHO + OH       <=> CHO + H2O        3.44E+09   1.18    -447. !86TSA/
HCHO + CH3      <=> CHO + CH4        5.54E+03   2.81    5862. !86TSA/
HCHO + CH3O     <=> CHO + CH3OH      1.02E+11   0.00    2981. !86TSA/
HCHO + HO2      <=> CHO + H2O2       1.58E+12   0.00   12665. !86TSA/
HCHO + O2       <=> CHO + HO2        2.05E+13   0.00   38949. !91TSA/
HCHO + CH3OO    <=> CHO + CH3OOH     1.99E+12   0.00   11665. !86TSA/
HCHO + CH2OH    <=> CHO + CH3OH      5.49E+03   2.80    5862. !87TSA/
HCHO + C2H3     <=> CHO + C2H4       5.43E+03   2.81    5862. !86TSA/
HCHO + C2H5     <=> CHO + C2H6       5.50E+03   2.81    5862. !86TSA/
HCHO            <=> CHO + H          6.27E+14  -1.651  50635. ! mtbe017d.mec avg err 10.69%
HCHO            <=> CO + H2          4.30E+20  -3.823  90631. ! mtbe017d.mec avg err  4.54%
CH4             <=> CH3 + H          5.11E+26  -4.845  51446. ! mtbe017d.mec avg err  8.39%
CH3 + O2        <=> CH3OO            9.79E+31  -5.575 109222. ! mtbe017d.mec avg err 12.75%
CH3 + O2        <=> CH3O + O         2.66E+35  -7.866   5504. ! mtbe017d.mec avg err  7.33%
CH3 + O2        <=> CH2OOH           7.83E+13  -.339   29880. ! mtbe017d.mec avg err 11.23%
CH3 + O2        <=> HCHO + OH        1.21E+07   .597   17237. ! mtbe017d.mec avg err  2.42%
CH3OO           <=> CH3O + O         3.38E+10   .613   18230. ! mtbe017d.mec avg err   .81%
CH3OO           <=> CH2OOH           1.32E+26  -4.932  60217. ! mtbe017d.mec avg err  4.49%
CH3OO           <=> HCHO + OH        3.00E+21  -4.531  48449. ! mtbe017d.mec avg err  3.71%
CH2OOH          <=> HCHO + OH        1.10E+25  -4.553  49469. ! mtbe017d.mec avg err  4.65%
CH3 + CH3       <=> C2H6             4.71E+10  -.519     686. ! mtbe017d.mec avg err  2.16%
CH3 + CH3       <=> C2H5 + H         4.17E+39  -8.223   8194. ! mtbe017d.mec avg err 42.15%
CH3 + CH3       <=> C2H4 + H2        5.73E+27  -5.129  16513. ! mtbe017d.mec avg err  5.69%
C2H6            <=> C2H5 + H         2.32E+30  -4.538  16851. ! mtbe017d.mec avg err  4.79%
C2H6            <=> C2H4 + H2        3.65E+52 -12.144 109762. ! mtbe017d.mec avg err 26.52%
CH3OO + OH      <=> CH3OH + O2       6.03E+13   0.00      0.   !86
CH3O + HO2      <=> HCHO + H2O2      3.01E+11   0.0       0.   !
CH3 + HO2       <=> CH3O + OH        1.35E+13   0.0       0. !16/09/
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CH3 + HO2       <=> CH4 + O2          3.61E-12   0.0       0. !86 TSA
CH3 + CH2OH     <=> CH4 + HCHO        2.41E-12   0.0       0. !86 TSA
CH3 + CH2OH     <=> CCOH              1.21E+12   0.0       0. !87 TSA
CH3 + CH3O      <=> CH4 + HCHO        2.41E+13   0.0       0. !86 TSA
CH3 + CH3OO     <=> CH3O + CH3O       2.41E+13   0.0       0. !86 TSA
OH + CH3O       <=> HCHO + H2O        1.81E+13   0.0       0. !86 TSA
OH + CH2OH      <=> HCHO + H2O        2.41E+13   0.0       0. !87 TSA
O + CH3OO       <=> CH3O + O2         3.61E+13   0.0       0. !86 TSA/
CH3O + CO       <=> CH3 + CO2         1.57E+13   0.00   11804. !86TSA/
O + CO          <=> CO2               1.82E+06   5.84    1632. !nist f
CO + H + M      <=> CHO + M           2.10E+20  -1.82    3688.    ! 2
CO + OH         <=> CO2 + H           6.32E+06   1.50    -497.    ! 2
CO + HO2        <=> CO2 + OH          1.51E+14   0.0    23648.    ! 2
CO + O2         <=> CO2 + O           2.53E+12   0.0    47693.    ! 2
OH + CH4        <=> CH3 + H2O         1.93E+05   2.40    2106. !86TSA/
O + CH4         <=> CH3 + OH          2.47E+07   1.96    7540. !modifi
H + CH4         <=> CH3 + H2          1.33E+04   3.00    8038. !92BAU/
O2 + CH2OH      <=> HCHO + HO2        1.21E+12   0.00       0. !87SA/H
CH3O + O2       <=> HO2 + HCHO        6.62E+10   0.00    2603. !86TSA/
CH3O + O        <=> OH + HCHO         6.03E+12   0.00       0. !86TSA/
HCO2H + O       <=> OH + HCO2.        1.15E+12   0.00    1351. !92 BAU
HCO2H + O       <=> OH + C.O2H        1.15E+12   0.00    1351. !92 BAU
HCO2H + H       <=> H2 + HCO2.        9.00E+12   0.00    3378. !92 BAU
HCO2H + H       <=> H2 + C.O2H        9.00E+12   0.00    3378. !92 BAU
HCO2H + OH      <=> H2O + HCO2.       2.71E+11   0.00       0. !92 BAU
HCO2H + OH      <=> H2O + C.O2H       2.71E+11   0.00       0. !92 BAU
C2H4 + HO2      <=> CH3CHO + OH       6.03E+09   0.0     7949.    !
C2H4 + CH3      <=> C2H3 + CH4        6.63E+00   3.7     9499.    !
C2H4 + O        <=> C2H3 + OH         5.55E+05   2.17    2597.    ! N
C2H4 + O        <=> CH3 + CHO         1.32E+08   1.55     427.    ! 8
C2H4 + O        <=> CH2 + HCHO        5.11E+10   0.66    1029.    ! N
C2H4 + O        <=> C.CHO + H         1.21E+06   2.08       0.    ! 9
C2H4 + O        <=> CYCOC             7.00E+11   0.00       0.    ! 7
C2H4 + OH       <=> C2H3 + H2O        1.57E+04   2.75    4173.    ! 8
C2H4 + H        <=> C2H3 + H2         1.33E+06   2.53   12241.    ! 8
C2H4 + CH3O     <=> C2H3 + CH3OH      6.63E+00   3.7     9499.    !
C2H4 + OH       <=> C.COH             3.09E+55 -11.747 110099. ! mtbe017d.mec avg err 24.25%
C2H4 + OH       <=> C*COH + H         1.41E+39  -8.532   7358. ! mtbe017d.mec avg err 15.25%
C2H4 + OH       <=> CCO.              1.19E+14   -.692   7744. ! mtbe017d.mec avg err  6.88%
C2H4 + OH       <=> CH3 + HCHO        3.07E+18  -3.378  14863. ! mtbe017d.mec avg err
11.87%
C2H4 + OH       <=> CH3CHO + H        2.57E+12   -.286  15123. ! mtbe017d.mec avg err  4.15%
C.COH           <=> C*COH + H         6.51E+11   -.075  14970. ! mtbe017d.mec avg err  4.08%
C.COH           <=> CCO.              2.73E+36  -8.222  38774. ! mtbe017d.mec avg err 10.58%
C.COH           <=> CH3 + HCHO        6.64E+35  -9.459  45167. ! mtbe017d.mec avg err 21.58%
C.COH           <=> CH3CHO + H        5.12E+30  -6.716  45565. ! mtbe017d.mec avg err  9.14%
CCO.            <=> C*COH + H         1.46E+30  -6.527  45406. ! mtbe017d.mec avg err  9.20%
CCO.            <=> CH3 + HCHO        2.26E+35  -9.343  34855. ! mtbe017d.mec avg err  7.36%
CCO.            <=> CH3CHO + H        5.25E+38  -8.874  21974. ! mtbe017d.mec avg err  5.25%
C.COH + O2      <=> COHCQ.            6.74E+36  -8.302  22429. ! mtbe017d.mec avg err  4.25%
C.COH + O2      <=> CO.COH + O        3.08E+37  -8.523   5206. ! mtbe017d.mec avg err 15.25%
C.COH + O2      <=> C*COHB + HO2B     2.44E+12   -.047  28994. ! mtbe017d.mec avg err
40.55%
C.COH + O2      <=> COHC.Q            1.32E+19  -2.353   5114. ! mtbe017d.mec avg err  5.12%
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C.COH + O2      <=> COHCHO + OH       2.09E+05    669   12291. ! mtbe017d.mec avg err
1.49%
C.COH + O2      <=> C.OHCQ          1.10E+09    .734   13290. ! mtbe017d.mec avg err  1.11%
C.COH + O2      <=> C*COH + HO2       3.76E+30   -6.441   5318. ! mtbe017d.mec avg err
12.03%
C.COH + O2      <=> CO.CQ           2.28E+26   -4.293   7242. ! mtbe017d.mec avg err  6.59%
C.COH + O2      <=> HCHO + CH2OOH     6.97E+32   -7.079   8230. ! mtbe017d.mec avg err
12.39%
COHCQ.        <=> CO.COH + O        1.29E+19   -2.264   9989 ! mtbe017d.mec avg err  9.46%
COHCQ.        <=> C*COHB + HO2B     3.79E+22   -3.896   59327. ! mtbe017d.mec avg err
21.28%
COHCQ.        <=> COHC.Q          1.83E+39   -8.855   33769. ! mtbe017d.mec avg err 10.64%
COHCQ.        <=> COHCHO + OH       1.81E+21   -1.720   44457. ! mtbe017d.mec avg err
17.72%
COHCQ.        <=> C.OHCQ          1.14E+25   -4.691   45443. ! mtbe017d.mec avg err 21.23%
COHCQ.        <=> C*COH + HO2       4.65E+47  -11.574   30911. ! mtbe017d.mec avg err  9.74%
COHCQ.        <=> CO.CQ           6.88E+46  -10.784   35240. ! mtbe017d.mec avg err 15.28%
COHCQ.        <=> HCHO + CH2OOH     4.66E+38   -9.218   26373. ! mtbe017d.mec avg err
21.96%
COHC.Q        <=> COHCHO + OH       2.88E+35   -7.622   41285. ! mtbe017d.mec avg err
10.92%
COHC.Q        <=> C.OHCQ          1.32E+09    -.052    -338. ! mtbe017d.mec avg err  2.59%
C.OHCQ        <=> COHCHO + OH       1.56E+09   -2.404    -777. ! mtbe017d.mec avg err  6.21%
C.OHCQ        <=> C*COH + HO2       4.77E+31   -7.433   14306. ! mtbe017d.mec avg err 11.55%
CO.CQ         <=> COHC.Q          4.00E+29   -5.993   17444. ! mtbe017d.mec avg err 18.64%
CO.CQ         <=> COHCHO + OH       6.32E+25   -6.156   31438. ! mtbe017d.mec avg err  7.76%
CO.CQ         <=> C.OHCQ          5.04E+29   -6.157   32463. ! mtbe017d.mec avg err  5.10%
CO.CQ         <=> C*COH + HO2       1.34E+46  -11.503   17348. ! mtbe017d.mec avg err 18.87%
CO.CQ         <=> HCHO + CH2OOH     5.07E+43  -10.044   21179. ! mtbe017d.mec avg err
24.93%
C2H4 + HO2      <=> C.CQ            4.52E+24   -3.942   22525. ! mtbe017d.mec avg err  7.36%
C2H4 + HO2      <=> C*CQ + H          3.62E+26   -5.224    9857. ! mtbe017d.mec avg err 17.92%
C2H4 + HO2      <=> CCQ.            3.18E+14    -.871   35949. ! mtbe017d.mec avg err  4.97%
C2H4 + HO2      <=> C2H4B + HO2B      2.13E+42   -9.886   20237. ! mtbe017d.mec avg err
22.06%
C2H4 + HO2      <=> CC.Q            8.62E+18   -2.212   21093. ! mtbe017d.mec avg err 11.59%
C2H4 + HO2      <=> CH3CHO + OH       4.23E+11   -1.096   27498. ! mtbe017d.mec avg err
2.69%
C.CQ + O2       <=> QCCQ.           3.33E+15   -1.057   28577. ! mtbe017d.mec avg err  3.47%
C.CQ + O2       <=> CO.CQ + O         9.75E+40   -9.490    6776. ! mtbe017d.mec avg err 15.39%
C.CQ + O2       <=> C*CQB + HO2B      4.86E+09    .810   29599. ! mtbe017d.mec avg err
137.69%
C.CQ + O2       <=> QCC.Q           1.81E+16   -1.608    8781. ! mtbe017d.mec avg err  5.79%
C.CQ + O2       <=> C*CQ + HO2        1.28E+24   -4.762    7467. ! mtbe017d.mec avg err 11.80%
C.CQ + O2       <=> QCCHO + OH        7.55E+08    .049    7064. ! mtbe017d.mec avg err  5.54%
QCCQ.         <=> CO.CQ + O         4.14E+26   -4.350    7908. ! mtbe017d.mec avg err 10.42%
QCCQ.         <=> C*CQB + HO2B      1.31E+23   -4.012   58994. ! mtbe017d.mec avg err 24.80%
QCCQ.         <=> QCC.Q           1.45E+37   -8.362   39708. ! mtbe017d.mec avg err 18.89%
QCCQ.         <=> C*CQ + HO2        3.13E+37   -9.194   30469. ! mtbe017d.mec avg err 25.19%
QCCQ.         <=> QCCHO + OH        8.80E+27   -6.252   35981. ! mtbe017d.mec avg err 18.67%
QCC.Q         <=> C*CQ + HO2        2.62E+40   -8.939   31235. ! mtbe017d.mec avg err 18.49%
QCC.Q         <=> QCCHO + OH        2.72E+09    -.455   19421. ! mtbe017d.mec avg err  4.10%
C.CHO + HO2     <=> QCCHO           2.13E+09    -.060    -320. ! mtbe017d.mec avg err  3.35%
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C.CHO + HO2      <=> QCC.*O + H       2.12E+38  -8.869   5172. ! mtbe017d.mec avg err
11.07%
C.CHO + HO2      <=> CHO + CH2OOH     6.68E-06   5.022  21956. ! mtbe017d.mec avg err
61.81%
C.CHO + HO2      <=> O*CCO. + OH      8.14E+00   3.586  16942. ! mtbe017d.mec avg err
11.15%
QCCHO          <=> QCC.*O + H       6.10E+14   -.507   1288. ! mtbe017d.mec avg err  .92%
QCCHO          <=> CHO + CH2OOH     5.44E+30  -6.242  91243. ! mtbe017d.mec avg err
9.07%
QCCHO          <=> O*CCO. + OH      7.27E+33  -6.704  85505. ! mtbe017d.mec avg err 9.37%
QCC.*O         <=> CH2OOH + CO      7.17E+48 -10.832  54367. ! mtbe017d.mec avg err
28.74%
O*CC*O         <=> CHO + CHO        2.02E+27  -5.374  14295. ! mtbe017d.mec avg err 22.59%
O*CC*O         <=> O*CC.*O + H      3.13E+47 -10.158  76840. ! mtbe017d.mec avg err 17.36%
O*CC.*O        <=> CHO + CO         2.04E+35  -7.663  86611. ! mtbe017d.mec avg err 9.24%
C*CQ           <=> C*CO. + OH       8.89E+13  -1.527   4233. ! mtbe017d.mec avg err 6.68%
CO.COH         <=> HCHO + CH2OH     2.94E+38  -8.577  23856. ! mtbe017d.mec avg err
25.23%
C2H4 + H       <=> C2H5             1.55E+32  -6.810  18611. ! mtbe017d.mec avg err 21.25%
C2H5 + O2      <=> CCQ.             5.57E+32  -6.242   7593. ! mtbe017d.mec avg err 24.24%
C2H5 + O2      <=> C2H4B + HO2B     2.14E+45 -10.791   8458. ! mtbe017d.mec avg err
15.64%
C2H5 + O2      <=> CCO. + O         6.88E+14  -1.072   5663. ! mtbe017d.mec avg err 4.98%
C2H5 + O2      <=> C.CQ             6.40E+13   -.395  28880. ! mtbe017d.mec avg err 11.69%
C2H5 + O2      <=> C2H4 + HO2       2.25E+28  -5.704   6281. ! mtbe017d.mec avg err 9.81%
C2H5 + O2      <=> CC.Q             5.45E+22  -3.222   7884. ! mtbe017d.mec avg err 7.86%
C2H5 + O2      <=> CH3CHO + OH      6.85E+05   .579  12187. ! mtbe017d.mec avg err 1.29%
CCQ.         <=> C2H4B + HO2B     4.52E+09   .640  13244. ! mtbe017d.mec avg err  .80%
CCQ.         <=> CCO. + O         2.02E+42  -9.824  40344. ! mtbe017d.mec avg err 14.91%
CCQ.         <=> C.CQ             8.93E+27  -5.531  61317. ! mtbe017d.mec avg err 14.90%
CCQ.         <=> CC.Q             5.69E+45 -10.950  36744. ! mtbe017d.mec avg err 12.08%
CCQ.         <=> CH3CHO + OH      8.74E+26  -6.452  46782. ! mtbe017d.mec avg err 13.46%
C.CQ         <=> CC.Q             7.10E+30  -6.430  47827. ! mtbe017d.mec avg err 16.01%
C.CQ         <=> CH3CHO + OH      7.39E+21  -5.925  11060. ! mtbe017d.mec avg err 28.94%
CC.Q         <=> CH3CHO + OH      2.39E+24  -5.514  11750. ! mtbe017d.mec avg err 35.18%
C2H2 + H       <=> C2H3             2.49E+09   -.150   -240. ! mtbe017d.mec avg err 2.00%
C2H3 + O2      <=> C*CQ.            4.58E+30  -5.820   7302. ! mtbe017d.mec avg err 14.42%
C2H3 + O2      <=> C*CO. + O        2.05E+35  -8.021   4606. ! mtbe017d.mec avg err 8.16%
C2H3 + O2      <=> C.*CQ            1.29E+15   -.762   1316. ! mtbe017d.mec avg err  .80%
C2H3 + O2      <=> C2H2 + HO2       3.24E+15  -2.156    663. ! mtbe017d.mec avg err 8.83%
C2H3 + O2      <=> CYC.OOC          1.09E+11   .071   2312. ! mtbe017d.mec avg err 2.75%
C2H3 + O2      <=> O*CCO.           5.47E+11  -1.575   1532. ! mtbe017d.mec avg err 2.14%
C2H3 + O2      <=> CHO + HCHO       1.69E+11  -1.356   -694. ! mtbe017d.mec avg err 9.94%
C2H3 + O2      <=> O*CC*O + H       2.43E+14  -1.056   1523. ! mtbe017d.mec avg err  .93%
C*CQ.        <=> C*CO. + O        2.30E+11   -.364    999. ! mtbe017d.mec avg err  .74%
C*CQ.        <=> C.*CQ            5.49E+44 -10.058  40558. ! mtbe017d.mec avg err 10.20%
C*CQ.        <=> C2H2 + HO2       1.32E+47 -11.592  42227. ! mtbe017d.mec avg err 4.58%
C*CQ.        <=> CYC.OOC          2.84E+41  -9.490  44347. ! mtbe017d.mec avg err 9.48%
C*CQ.        <=> O*CCO.           4.87E+39 -10.314  39851. ! mtbe017d.mec avg err 13.77%
C*CQ.        <=> CHO + HCHO       4.55E+38  -9.918  37484. ! mtbe017d.mec avg err 6.04%
C*CQ.        <=> O*CC*O + H       2.09E+42  -9.798  39836. ! mtbe017d.mec avg err 11.92%
C.*CQ        <=> C2H2 + HO2       2.45E+40  -9.505  39599. ! mtbe017d.mec avg err 11.10%
C.*CQ        <=> CYC.OOC          2.59E+22  -4.141  12061. ! mtbe017d.mec avg err 15.75%
C.*CQ        <=> O*CCO.           6.89E+22  -5.894  13686. ! mtbe017d.mec avg err 12.41%
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C.*CQ          <=> CHO + HCHO        1.42E-22  -5.607  11531. ! mtbe017d.mec avg err 26.80%
C.*CQ          <=> O*CC*O + H        2.01E-25  -5.320  13724. ! mtbe017d.mec avg err 14.54%
CYC.OOC          <=> O*CCO.          1.47E-22  -4.631  13117. ! mtbe017d.mec avg err 17.57%
CYC.OOC          <=> CHO + HCHO        3.63E-11  -1.928    142. ! mtbe017d.mec avg err 11.68%
CYC.OOC          <=> O*CC*O + H       8.14E+13  -1.411   2182. ! mtbe017d.mec avg err  1.02%
O*CCO.         <=> CHO + HCHO        5.24E+08   -.124   1214. ! mtbe017d.mec avg err  2.44%
O*CCO.         <=> O*CC*O + H        2.75E+21  -3.775   9003. ! mtbe017d.mec avg err 16.80%
C2H2 + OH        <=> C.*COH          3.80E+13  -1.490  24384. ! mtbe017d.mec avg err 11.86%
C2H2 + OH        <=> C#COH + H         4.80E+36  -7.927   7481. ! mtbe017d.mec avg err 11.46%
C2H2 + OH        <=> C*CO.           3.69E+12   -.206  14335. ! mtbe017d.mec avg err  2.42%
C2H2 + OH        <=> C*C*O + H         6.58E+21  -3.384   5119. ! mtbe017d.mec avg err  7.48%
C2H2 + OH        <=> C.CHO           2.34E+13   -.672   3926. ! mtbe017d.mec avg err  5.41%
C2H2 + OH        <=> CH3C.*O           7.91E+18  -2.680   3870. ! mtbe017d.mec avg err  6.74%
C2H2 + OH        <=> CH3 + CO          4.32E+27  -6.066   7082. ! mtbe017d.mec avg err  5.87%
C.*COH         <=> C#COH + H         2.92E+26  -4.481   8176. ! mtbe017d.mec avg err 19.13%
C.*COH         <=> C*CO.           1.12E+31  -6.609  50029. ! mtbe017d.mec avg err 12.18%
C.*COH         <=> C*C*O + H         6.86E+39  -9.202  37882. ! mtbe017d.mec avg err 12.36%
C.*COH         <=> C.CHO           8.69E+35  -8.052  37942. ! mtbe017d.mec avg err 10.85%
C.*COH         <=> CH3C.*O           4.82E+36  -8.420  36565. ! mtbe017d.mec avg err 10.97%
C.*COH         <=> CH3 + CO          8.23E+43 -11.377  39334. ! mtbe017d.mec avg err  9.46%
C*CO.          <=> C*C*O + H         4.19E+43 -10.087  40679. ! mtbe017d.mec avg err 23.59%
C*CO.          <=> C.CHO           3.87E+20  -2.762  39499. ! mtbe017d.mec avg err  4.91%
C*CO.          <=> CH3C.*O           1.15E+14  -1.602    641. ! mtbe017d.mec avg err  1.22%
C*CO.          <=> CH3 + CO          4.29E+26  -5.421  36187. ! mtbe017d.mec avg err  4.49%
C.CHO          <=> CH3C.*O           8.01E+24  -3.754  37304. ! mtbe017d.mec avg err 18.20%
C.CHO          <=> CH3 + CO          6.61E+23  -4.727  38065. ! mtbe017d.mec avg err  3.44%
C.CHO          <=> C*C*O + H         1.37E+22  -3.076  39191. ! mtbe017d.mec avg err 16.95%
CH3C.*O          <=> CH3 + CO          1.67E+12   -.814  41162. ! mtbe017d.mec avg err 15.20%
CH3C.*O          <=> C*C*O + H         2.58E+26  -5.159  15922. ! mtbe017d.mec avg err  9.32%
COC + O          <=> COC. + OH         5.00E+13   0.0    4571.    !
COC + H          <=> COC. + H2         6.41E+00   4.13   2180.    !
COC + OH         <=> COC. + H2O        6.27E+12   0.0     739.    !
COC + CH3        <=> COC. + CH4        3.55E+12   0.0   11800.    !
COC + CH3O       <=> COC. + CH3OH      3.55E+12   0.0   11800.    !
CH3O + CH3       <=> COC             5.96E+18  -3.062  45056. ! mtbe017d.mec avg err  5.05%
CH3O + CH3       <=> COC. + H          7.34E+34  -6.820   7124. ! mtbe017d.mec avg err 47.68%
CH3O + CH3       <=> CH2S + CH3OH      1.94E+14   -.314  19135. ! mtbe017d.mec avg err
12.00%
COC            <=> COC. + H          2.10E+15   -.437  19034. ! mtbe017d.mec avg err 11.79%
COC            <=> CH2S + CH3OH      7.80E+45  -9.746 104606. ! mtbe017d.mec avg err 27.78%
COC.           <=> HCHO + CH3        1.01E+47  -9.881 104547. ! mtbe017d.mec avg err 27.88%
COC. + O2        <=> COCQ.           3.09E+28  -5.789  15191. ! mtbe017d.mec avg err 19.66%
COC. + O2        <=> C.OCQ           1.29E+37  -8.005   6211. ! mtbe017d.mec avg err 12.41%
COC. + O2        <=> HCHO + CH2OOH     1.19E+34  -6.912   8351. ! mtbe017d.mec avg err
14.39%
COCQ.          <=> C.OCQ           3.14E+27  -4.269  10684. ! mtbe017d.mec avg err 14.64%
COCQ.          <=> HCHO + CH2OOH     2.24E+36  -7.972  26426. ! mtbe017d.mec avg err
20.43%
C.OCQ          <=> HCHO + CH2OOH     8.58E+42  -9.344  41597. ! mtbe017d.mec avg err
17.04%
C*CC. + C2C*C      <=> CC*C + C2.C*C      2.01E-01   4.00    227.    !
C*CC. + HCHO       <=> CHO + CC*C        1.26E+08   1.90  18191. !86TSA
C*CC. + C3COC      <=> CC*C + C3.COC      3.56E+02   3.30  19844. !91 TS
C*CC. + C3COC      <=> CC*C + C3COC.      1.74E+03   2.90  19314. !A fro
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C*CC. + CH3OH      <=> CC*C + CH2OH        1.74E+03   2.90   20456. !91 TS
C*CC. + C2C*O      <=> CC*C + C2.C*O       7.08E+11   0.00   16492. !89 LO
C*CC. + O2         <=> C*C*C + HO2         1.21E+12   0.00   13553. !91 TS
C*CC. + C2CYCOC    <=> CC*C + C2CYCOC.     1.00E-00   4.00   13318. !AMD C
C*CC. + CCYCOC     <=> CC*C + CCYC.OC      4.42E+01   3.30   17169. !91TSA
C*CC. + C*CICC*O   <=> CC*C + C*CICC.*O    1.90E+11   0.00   6218. !A=1/2
C*CC  + C2CC*O     <=> CC*C + C2CC.*O      3.80E+11   0.00   7218. ! the
C*CC. + O*CC*O     <=> CC*C + O*CC.*O      7.90E+11   0.00   7218. ! 2*(c
C*CC. + CCC*O      <=> CC*C + CCC.*O       3.80E+11   0.00   7218. ! the
C*CC. + CH3CHO     <=> CC*C + CH3C.*O      3.80E+11   0.00   7218. ! 89 L
C*CC. + C2CQC*O    <=> CC*C + C2CQC.*O     1.90E+11   0.00   7218. ! 1/2
C*CC. + C2COHC*O   <=> CC*C + C2COHC.*O    1.90E+11   0.00   7218. ! 1/2
C*CC. + CCQCHO     <=> CC*C + CCQC.*O      1.90E+11   0.00   7218. ! 1/2
C*CC. + CCOHCHO    <=> CC*C + CCOHC.*O     1.90E+11   0.00   7218. ! 1/2
CC*C + O       <=> C*CC. + OH          6.03E+10   0.70   7633. !91TSA
CC*C + O       <=> CCYCOC              4.20E+12   0.00   503. !73HER
CC*C + H       <=> C*CC. + H2          1.75E+05   2.50   2492. !91TSA
CC*C + H       <=> C2H4 + CH3          7.23E+12   0.00   1302. !91TSA
CC*C + OH      <=> C*CC. + H2O         3.12E+06   2.00   -298. !91TSA
CC*C + CH3     <=> C*CC. + CH4         2.21E+00   3.50   5675. !91TSA
CC*C + CH3O    <=> C*CC. + CH3OH       2.21E+00   3.50   5675. !91TSA
CC*C + HO2     <=> C*CC. + H2O2        9.64E+03   2.60   13910. !91TSA
CC*C + HO2     <=> CCYCOC + OH         1.05E+12   0.00   14206. !91TSA
CC*C + O2      <=> C*CC. + HO2         1.95E+12   0.00   39110. !R.W.W
CC.C + O2      <=> C2CQ.           2.90E+28  -5.259  25035. ! mtbe017d.mec avg err  9.28%
CC.C + O2      <=> CC*CB + HO2B        1.82E+49  -11.956   9442. ! mtbe017d.mec avg err
20.72%
CC.C + O2      <=> C2C.Q           5.06E+17  -1.718   8038. ! mtbe017d.mec avg err  7.37%
CC.C + O2      <=> C2C*O + OH          4.84E+08   -.245  12041. ! mtbe017d.mec avg err  1.17%
CC.C + O2      <=> C2.CQ           1.49E+11   .037   12664. ! mtbe017d.mec avg err  2.54%
CC.C + O2      <=> CCYCOC + OH         2.13E+33  -7.124   8861. ! mtbe017d.mec avg err
12.69%
CC.C + O2      <=> CC*C + HO2          6.24E+17  -2.221  10575. ! mtbe017d.mec avg err  7.34%
CC.C + O2      <=> C*CQ + CH3          3.21E+27  -4.564  10895. ! mtbe017d.mec avg err 12.31%
C2CQ.          <=> CC*CB + HO2B        1.31E+08   .870   17572. ! mtbe017d.mec avg err  .77%
C2CQ.          <=> C2C.Q           1.50E+46 -10.814  41672. ! mtbe017d.mec avg err 21.63%
C2CQ.          <=> C2C*O + OH          4.96E+32  -8.127  46104. ! mtbe017d.mec avg err 24.48%
C2CQ.          <=> C2.CQ           1.53E+35  -7.857  46685. ! mtbe017d.mec avg err 28.96%
C2CQ.          <=> CCYCOC + OH         2.53E+54 -13.557  39427. ! mtbe017d.mec avg err 15.48%
C2CQ.          <=> C*CQ + CH3          8.72E+45 -11.254  44702. ! mtbe017d.mec avg err 26.45%
C2C.Q          <=> C2.CQ           2.41E+28  -5.978  50817. ! mtbe017d.mec avg err 28.16%
C2.CQ          <=> C2C*O + OH          1.24E+13  -3.580   126. ! mtbe017d.mec avg err  8.58%
C2.CQ          <=> CCYCOC + OH         3.14E+38  -9.865  14698. ! mtbe017d.mec avg err 33.54%
C2.CQ          <=> C*CQ + CH3          8.35E+19  -3.561  19789. ! mtbe017d.mec avg err 22.73%
C*CC. + O2     <=> C*CCQ.              1.59E+13  -1.257  31670. ! mtbe017d.mec avg err 19.50%
C*CC. + O2     <=> C*CCO. + O          3.48E+34  -7.593   5724. ! mtbe017d.mec avg err 12.47%
C*CC. + O2     <=> C*C.CQ              2.64E+17  -1.255  42868. ! mtbe017d.mec avg err  3.72%
C*CC. + O2     <=> C.*CCQ              1.59E+12   -.153  17303. ! mtbe017d.mec avg err  4.41%
C*CC. + O2     <=> C*CC.Q              6.73E+12   -.239  15252. ! mtbe017d.mec avg err  4.40%
C*CC. + O2     <=> C*CC*O + OH         1.35E+08   -.106  20031. ! mtbe017d.mec avg err  7.46%
C*CC. + O2     <=> YC.COOC             1.50E+13   -.090  20971. ! mtbe017d.mec avg err  4.32%
C*CC. + O2     <=> C.CYCOOC            6.23E+29  -6.640  17289. ! mtbe017d.mec avg err 14.19%
C*CC. + O2     <=> CO.CYCOC            6.16E+13  -1.998  13881. ! mtbe017d.mec avg err  6.03%
```

```
C*CC. + O2      <=> CYC.OC+HCHO      1.67E+16  -1.631  16986. ! mtbe017d.mec avg err
5.14%
C*CC. + O2      <=> YCC.OOC          1.08E+20  -2.714  18117. ! mtbe017d.mec avg err  9.52%
C*CC. + O2      <=> CCYC.OOC         1.93E+03   1.089  20427. ! mtbe017d.mec avg err 16.43%
C*CC. + O2      <=> CCYCOOC.         2.75E+03    .680  35359. ! mtbe017d.mec avg err  5.30%
C*CC. + O2      <=> C*COOC.          2.17E+03    .743  33376. ! mtbe017d.mec avg err  5.59%
C*CC. + O2      <=> C*CO. + HCHO     1.51E+08   -.678  37094. ! mtbe017d.mec avg err  5.61%
C*CC. + O2      <=> O*CCCO.          4.47E+08    .324  36618. ! mtbe017d.mec avg err  5.73%
C*CC. + O2      <=> C.CHO + HCHO     1.44E-01   2.468  16925. ! mtbe017d.mec avg err
10.28%
C*CC. + O2      <=> CC*OCO.          1.19E+05   1.806  20226. ! mtbe017d.mec avg err 14.15%
C*CC. + O2      <=> CH3C.*O + HCHO   6.97E-02   1.999  32308. ! mtbe017d.mec avg err
8.61%
C*CC. + O2      <=> CCO.C*O          8.19E+05   1.275  35565. ! mtbe017d.mec avg err  5.24%
C*CC. + O2      <=> CH3CHO + CHO     1.24E-01   2.095  30988. ! mtbe017d.mec avg err
7.96%
C*CC. + O2      <=> CCOHC.*O         2.49E+06   1.218  33694. ! mtbe017d.mec avg err  6.17%
C*CCQ.          <=> C*CCO. + O       4.51E-03   3.525  32815. ! mtbe017d.mec avg err  5.20%
C*CCQ.          <=> C*C.CQ           2.15E+22  -3.561  60583. ! mtbe017d.mec avg err 20.50%
C*CCQ.          <=> C.*CCQ           1.08E+22  -3.825  35436. ! mtbe017d.mec avg err 18.38%
C*CCQ.          <=> C*CC.Q           3.75E+23  -4.170  33510. ! mtbe017d.mec avg err 18.64%
C*CCQ.          <=> C*CC*O + OH      5.12E+16  -3.417  38048. ! mtbe017d.mec avg err 14.64%
C*CCQ.          <=> YC.COOC          6.04E+21  -3.415  38979. ! mtbe017d.mec avg err 18.28%
C*CCQ.          <=> C.CYCOOC         1.76E+39 -10.062  35520. ! mtbe017d.mec avg err 36.52%
C*CCQ.          <=> CO.CYCOC         9.90E+23  -5.717  32228. ! mtbe017d.mec avg err 23.10%
C*CCQ.          <=> CYC.OC+HCHO      1.56E+26  -5.331  35116. ! mtbe017d.mec avg err
17.56%
C*CCQ.          <=> YCC.OOC          5.00E+29  -6.309  36088. ! mtbe017d.mec avg err 13.94%
C*CCQ.          <=> CCYC.OOC         6.05E+10  -1.946  37762. ! mtbe017d.mec avg err 10.73%
C*CCQ.          <=> CCYCOOC.         8.72E+08  -1.802  52967. ! mtbe017d.mec avg err 18.34%
C*CCQ.          <=> C*COOC.          1.31E+09  -1.816  51011. ! mtbe017d.mec avg err 18.15%
C*CCQ.          <=> C*CO. + HCHO     3.16E+13  -3.108  54676. ! mtbe017d.mec avg err 17.54%
C*CCQ.          <=> O*CCCO.          9.21E+13  -2.106  54190. ! mtbe017d.mec avg err 17.77%
C*CCQ.          <=> C.CHO + HCHO     4.25E+06   -.553  34272. ! mtbe017d.mec avg err 26.34%
C*CCQ.          <=> CC*OCO.          3.55E+12  -1.225  37548. ! mtbe017d.mec avg err 12.99%
C*CCQ.          <=> CH3C.*O + HCHO   1.88E+04   -.458  49905. ! mtbe017d.mec avg err
31.86%
C*CCQ.          <=> CCO.C*O          2.60E+11  -1.207  53173. ! mtbe017d.mec avg err 18.40%
C*CCQ.          <=> CH3CHO + CHO     6.18E+04   -.435  48606. ! mtbe017d.mec avg err
20.18%
C*CCQ.          <=> CCOHC.*O         1.37E+12  -1.328  51316. ! mtbe017d.mec avg err 17.58%
C*CC.Q          <=> C*C.CQ           3.62E+03    .914  50440. ! mtbe017d.mec avg err 19.49%
C*CC.Q          <=> C.*CCQ           3.05E-05   3.120  28140. ! mtbe017d.mec avg err 77.16%
C*CC.Q          <=> C*CC*O + OH      1.04E+07   -.204  29928. ! mtbe017d.mec avg err 71.79%
C*CC.Q          <=> YC.COOC          1.37E+10   -.367    234. ! mtbe017d.mec avg err  2.84%
C*CC.Q          <=> C.CYCOOC         3.28E+11  -3.555    540. ! mtbe017d.mec avg err  8.68%
YC.COOC         <=> C*C.CQ           7.43E+05  -1.819   -374. ! mtbe017d.mec avg err 13.13%
YC.COOC         <=> C.*CCQ           2.67E+18  -2.872  42303. ! mtbe017d.mec avg err 12.74%
YC.COOC         <=> C.CYCOOC         5.99E+19  -3.149  41064. ! mtbe017d.mec avg err 13.39%
YC.COOC         <=> CO.CYCOC         1.04E-08   2.766  10413. ! mtbe017d.mec avg err 104.85%
YC.COOC         <=> CYC.OC+HCHO      1.72E+36  -9.012  26326. ! mtbe017d.mec avg err
17.31%
YC.COOC         <=> YCC.OOC          1.15E+40  -8.860  29217. ! mtbe017d.mec avg err 13.14%
YC.COOC         <=> O*CCCO.          2.27E-21   7.435  10168. ! mtbe017d.mec avg err 42.25%
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YC.COOC      <=> C.CHO + HCHO      4.41E-23   8.308   11966. ! mtbe017d.mec avg err
53.12%
C.CYCOOC     <=> C*C.CQ           1.19E-16   7.489   15715. ! mtbe017d.mec avg err 72.57%
C.CYCOOC     <=> C.*CCQ           1.14E+02   1.808   17601. ! mtbe017d.mec avg err 6.49%
C.CYCOOC     <=> CO.CYCOC          7.50E+02   1.680   16170. ! mtbe017d.mec avg err
6.33%
C.CYCOOC     <=> CYC.OC+HCHO       6.71E+18  -2.995    6878. ! mtbe017d.mec avg err
19.89%
C.CYCOOC     <=> CCYC.OOC          7.33E+12  -2.302    4295. ! mtbe017d.mec avg err
60.09%
C.CYCOOC     <=> CCYCOOC.          3.53E+48  14.262  -11146. ! mtbe017d.mec avg err
114.33%
C.CYCOOC     <=> C*COOC.           2.30E+46  13.846  -10579. ! mtbe017d.mec avg err
101.93%
C.CYCOOC     <=> C*CO. + HCHO      5.34E-53  15.812  -11418. ! mtbe017d.mec avg err
93.30%
C.CYCOOC     <=> CC*OCO.           5.05E-54  17.285  -11876. ! mtbe017d.mec avg err 91.63%
C.CYCOOC     <=> CH3C.*O + HCHO     3.13E-64  19.090  -16212. ! mtbe017d.mec avg err
120.87%
C.CYCOOC     <=> CCO.C*O           1.30E-58  18.809  -13199. ! mtbe017d.mec avg err 95.55%
C.CYCOOC     <=> CH3CHO + CHO       6.19E-62  18.679  -14762. ! mtbe017d.mec avg err
97.62%
C.CYCOOC     <=> CCOHC.*O          1.86E-55  18.055  -12178. ! mtbe017d.mec avg err
86.93%
CO.CYCOC     <=> C*C.CQ           3.89E-68  21.575  -13491. ! mtbe017d.mec avg err 89.50%
CO.CYCOC     <=> C.*CCQ           3.23E+03   1.146   61489. ! mtbe017d.mec avg err 8.67%
CO.CYCOC     <=> CYC.OC+HCHO       3.90E+04    .946   60279. ! mtbe017d.mec avg err
8.61%
YCC.OOC      <=> O*CCCO.          9.96E+24  -4.774   11834. ! mtbe017d.mec avg err 32.36%
YCC.OOC      <=> C.CHO + HCHO       2.66E+09  -1.097   -1632. ! mtbe017d.mec avg err
13.30%
CCYC.OOC     <=> CCYCOOC.          7.17E+12  -1.062    1146. ! mtbe017d.mec avg err 1.73%
CCYC.OOC     <=> CC*OCO.           2.48E-11   2.334   -4642. ! mtbe017d.mec avg err 77.30%
CCYC.OOC     <=> CH3C.*O + HCHO     1.55E+05   -.157   -3175. ! mtbe017d.mec avg err
10.09%
CCYCOOC.     <=> CCO.C*O           8.39E+10   -.516    -160. ! mtbe017d.mec avg err 1.11%
CCYCOOC.     <=> CH3CHO + CHO       6.15E+04    .032   -2585. ! mtbe017d.mec avg err
4.45%
CCYCOOC.     <=> CCOHC.*O          1.76E+11   -.613     -27. ! mtbe017d.mec avg err 1.79%
C*COOC.     <=> C*CO. + HCHO       6.25E-03   3.015   -1600. ! mtbe017d.mec avg err 1.80%
O*CCCO.     <=> C.CHO + HCHO       2.81E+12   -.964     607. ! mtbe017d.mec avg err 3.78%
CCO.C*O     <=> CH3CHO + CHO       9.43E+19  -3.342    8106. ! mtbe017d.mec avg err
25.08%
CCO.C*O     <=> CCOHC.*O          2.93E+12  -1.141    2225. ! mtbe017d.mec avg err 14.41%
C.*CCQ      <=> C2H2 + CH2OOH      3.66E+05   1.005   25146. ! mtbe017d.mec avg err
4.38%
C*C.CQ      <=> C*C*C + HO2       2.71E+39  -8.393   38687. ! mtbe017d.mec avg err 17.03%
CC*C + H     <=> CC.C            1.48E+28  -5.550   17004. ! mtbe017d.mec avg err 18.84%
CC*C + HO2    <=> C2.CQ           2.44E+34  -6.780    8016. ! mtbe017d.mec avg err 31.39%
CC*C + HO2    <=> CCYCOC + OH       2.33E+20  -3.123   10686. ! mtbe017d.mec avg err
22.54%
CC*C + HO2    <=> C*CQ + CH3        1.31E+08    .995   17590. ! mtbe017d.mec avg err 3.29%
CC*C + HO2    <=> C2CQ.           1.35E+08   1.336   30846. ! mtbe017d.mec avg err 6.73%
CC*C + HO2    <=> CC.CQ           6.13E+45 -11.037   23886. ! mtbe017d.mec avg err 28.27%
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CC*C + HO2      <=> CCYCOC + OH       4.47E+25  -5.202   8361. ! mtbe017d.mec avg err
32.03%
CC*C + HO2      <=> CCCQ.             4.42E+12   -.602  16285. ! mtbe017d.mec avg err  2.14%
CC*C + HO2      <=> CCC. + O2         3.23E+46 -11.560  22047. ! mtbe017d.mec avg err 20.41%
CC.CQ         <=> CCYCOC + OH       3.61E+26  -4.474  24573. ! mtbe017d.mec avg err 13.65%
CC.CQ         <=> CCCQ.           1.56E+16  -2.469  18164. ! mtbe017d.mec avg err 23.49%
CC.CQ         <=> CC*CB + HO2B      4.25E+45 -11.818  22377. ! mtbe017d.mec avg err  5.73%
CC.CQ         <=> CCC. + O2         1.00E+26  -5.703  25530. ! mtbe017d.mec avg err  9.77%
CCCQ.         <=> CC*CB + HO2B      5.67E+28  -5.882  26566. ! mtbe017d.mec avg err  9.78%
CCCQ.         <=> CCC. + O2         5.25E+43 -10.239  38434. ! mtbe017d.mec avg err 19.63%
C2.CQ + O2      <=> CCQCQ.            1.64E+48 -10.949  40647. ! mtbe017d.mec avg err 18.57%
C2.CQ + O2      <=> C*CQCB + HO2B     3.08E+32  -6.810   4905. ! mtbe017d.mec avg err
5.82%
C2.CQ + O2      <=> C.CQCQ            1.03E+16  -1.477  11272. ! mtbe017d.mec avg err  9.18%
C2.CQ + O2      <=> C*CCQ + HO2       2.12E+33  -7.185  10027. ! mtbe017d.mec avg err
8.55%
C2.CQ + O2      <=> C*CQ +CH2OOH      3.36E+29  -5.250  13311. ! mtbe017d.mec avg err
11.50%
C2.CQ + O2      <=> CQCYCOC + OH      3.41E+17  -1.984  23185. ! mtbe017d.mec avg err
6.14%
C2.CQ + O2      <=> QCYCCOC + OH      2.55E+23  -3.855  14417. ! mtbe017d.mec avg err
9.28%
C2.CQ + O2      <=> CC.QCQ          9.13E+25  -4.810  13527. ! mtbe017d.mec avg err 10.86%
C2.CQ + O2      <=> YCOCICQ + OH      1.08E+24  -4.565   8746. ! mtbe017d.mec avg err
15.81%
C2.CQ + O2      <=> CC*OCQ + OH       7.40E+09   -.116   9270. ! mtbe017d.mec avg err  9.88%
C2.CQ + O2      <=> C*CQC + HO2       2.73E+25  -3.934   8899. ! mtbe017d.mec avg err
12.21%
C2.CQ + O2      <=> CCQC.Q            1.45E+09    .289   9730. ! mtbe017d.mec avg err  9.38%
C2.CQ + O2      <=> CCQCHO + OH       1.68E+10   -.690  17209. ! mtbe017d.mec avg err
8.52%
C2.CQ + O2      <=> CC*CQ + HO2       5.90E+12   -.215  17566. ! mtbe017d.mec avg err  4.29%
C2.CQ + O2      <=> CCQ.CQ            7.42E-02   3.125  17225. ! mtbe017d.mec avg err  4.01%
C2.CQ + O2      <=> CC*CQB + HO2B     3.50E+42  -9.843  14007. ! mtbe017d.mec avg err
32.43%
CCQCQ.        <=> C*CQCB + HO2B     2.42E+32  -6.264  22215. ! mtbe017d.mec avg err
43.32%
CCQCQ.        <=> C.CQCQ          3.17E+29  -5.844  37771. ! mtbe017d.mec avg err  6.45%
CCQCQ.        <=> C*CCQ + HO2       3.15E+47 -11.518  32702. ! mtbe017d.mec avg err
29.48%
CCQCQ.        <=> C*CQ +CH2OOH      4.09E+46 -10.576  40354. ! mtbe017d.mec avg err
9.11%
CCQCQ.        <=> CQCYCOC + OH      3.28E+27  -5.302  51853. ! mtbe017d.mec avg err
16.91%
CCQCQ.        <=> QCYCCOC + OH      3.84E+39  -8.938  42663. ! mtbe017d.mec avg err
12.31%
CCQCQ.        <=> CC.QCQ          8.36E+42 -10.108  40989. ! mtbe017d.mec avg err  9.76%
CCQCQ.        <=> YCOCICQ + OH      1.29E+31  -7.107  26247. ! mtbe017d.mec avg err
21.50%
CCQCQ.        <=> CC*OCQ + OH       5.06E+19  -3.491  32579. ! mtbe017d.mec avg err  3.72%
CCQCQ.        <=> C*CQC + HO2       1.81E+32  -6.414  26544. ! mtbe017d.mec avg err 15.38%
CCQCQ.        <=> CCQC.Q          4.66E+19  -3.277  34023. ! mtbe017d.mec avg err  5.03%
CCQCQ.        <=> CCQCHO + OH       2.56E+22  -4.658  46060. ! mtbe017d.mec avg err
7.15%
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CCQCQ.          <=> CC*CQ + HO2        5.47E+24  -4.132  46306. ! mtbe017d.mec avg err 13.26%
CCQCQ.          <=> CCQ.CQ             1.47E+08   -.094  44841. ! mtbe017d.mec avg err 14.32%
CCQCQ.          <=> C*CCQB + HO2B      4.05E+35  -8.078  24842. ! mtbe017d.mec avg err
42.60%
CCQCQ.          <=> CC*CQB + HO2B      3.73E+39  -8.590  46843. ! mtbe017d.mec avg err
30.63%
C.CQCQ          <=> C*CCQ + HO2        2.22E+39  -8.589  47354. ! mtbe017d.mec avg err 29.37%
C.CQCQ          <=> C*CQ +CH2OOH       2.56E+66 -17.416  29411. ! mtbe017d.mec avg err
63.66%
C.CQCQ          <=> CQCYCOC + OH       6.33E+74 -22.878  45711. ! mtbe017d.mec avg err
34.30%
C.CQCQ          <=> QCYCCOC + OH       3.05E+70 -19.332  35570. ! mtbe017d.mec avg err
57.80%
C.CQCQ          <=> CC.QCQ             7.90E+65 -17.953  31236. ! mtbe017d.mec avg err 62.51%
C.CQCQ          <=> CC*OCQ + OH        1.58E+65 -18.212  32043. ! mtbe017d.mec avg err
95.72%
C.CQCQ          <=> CCQC.Q             9.66E+67 -18.044  32661. ! mtbe017d.mec avg err 85.27%
C.CQCQ          <=> CCQCHO + OH        4.80E+42 -13.159  12526. ! mtbe017d.mec avg err
95.83%
C.CQCQ          <=> CCQ.CQ             3.75E+46 -13.161  13877. ! mtbe017d.mec avg err 90.86%
CC.QCQ          <=> YCOCICQ + OH       2.24E+65 -17.684  31148. ! mtbe017d.mec avg err
88.46%
CC.QCQ          <=> CC*OCQ + OH        4.43E+10   -.756  19901. ! mtbe017d.mec avg err  3.78%
CC.QCQ          <=> C*CQC + HO2        2.16E+10   -.331   -47. ! mtbe017d.mec avg err  3.79%
CC.QCQ          <=> CCQC.Q             2.44E+11   -.738  22172. ! mtbe017d.mec avg err  3.89%
CC.QCQ          <=> CCQCHO + OH        5.27E-51  15.533   4713. ! mtbe017d.mec avg err
******%
CC.QCQ          <=> CCQ.CQ             6.06E-37  12.723  12269. ! mtbe017d.mec avg err 729.06%
CCQC.Q          <=> CCQCHO + OH        1.14E+31  -7.576  27424. ! mtbe017d.mec avg err
88.84%
CCQC.Q          <=> CC*CQ + HO2        2.99E+09   -.096   -297. ! mtbe017d.mec avg err  6.00%
CCQC.Q          <=> CCQ.CQ             1.09E+10   -.605  19607. ! mtbe017d.mec avg err  5.99%
CCQ.CQ          <=> CC*OCQ + OH        6.12E-56  16.518 -15506. ! mtbe017d.mec avg err
125.85%
CCQ.CQ          <=> CCQCHO + OH        5.36E+38  -8.274  36744. ! mtbe017d.mec avg err
62.28%
CCQ.CQ          <=> C*CCQB + HO2B      2.98E+38  -8.369  55194. ! mtbe017d.mec avg err
14.52%
CCQ.CQ          <=> CC*CQB + HO2B      6.36E+27  -4.652  38953. ! mtbe017d.mec avg err
22.15%
CC.CQ + O2      <=> CCQ.CQ             5.64E+27  -4.696  39632. ! mtbe017d.mec avg err 21.51%
CC.CQ + O2      <=> C*CCQB + HO2B      9.14E+37  -8.378   6444. ! mtbe017d.mec avg err
4.14%
CC.CQ + O2      <=> CC*CQB + HO2B      3.87E+19  -2.247  11731. ! mtbe017d.mec avg err
10.04%
CC.CQ + O2      <=> C.CQCQ             9.22E+18  -2.126  11946. ! mtbe017d.mec avg err  9.72%
CC.CQ + O2      <=> C*CCQ + HO2        7.96E+31  -6.729  10281. ! mtbe017d.mec avg err
8.17%
CC.CQ + O2      <=> C*CQ +CH2OOH       3.09E+30  -5.406  14562. ! mtbe017d.mec avg err
14.58%
CC.CQ + O2      <=> CQCYCOC + OH       3.47E+16  -1.584  22874. ! mtbe017d.mec avg err
11.84%
CC.CQ + O2      <=> QCYCCOC + OH       5.14E+23  -3.826  15111. ! mtbe017d.mec avg err
11.95%
```

```
CC.CQ + O2      <=> CC.QCQ          5.96E+26  -4.925  14638. ! mtbe017d.mec avg err 13.86%
CC.CQ + O2      <=> YCOCICQ + OH     4.74E+13  -1.639  15823. ! mtbe017d.mec avg err
5.49%
CC.CQ + O2      <=> CC*OCQ + OH      4.84E+00   2.481  15158. ! mtbe017d.mec avg err
3.24%
CC.CQ + O2      <=> C*CQC + HO2      1.87E+15  -1.061  15953. ! mtbe017d.mec avg err
5.84%
CC.CQ + O2      <=> CCQC.Q          5.94E-01   2.942  15219. ! mtbe017d.mec avg err  2.76%
CC.CQ + O2      <=> CCQCHO + OH      1.76E+27  -5.633   9810. ! mtbe017d.mec avg err
18.21%
CC.CQ + O2      <=> CC*CQ + HO2      2.59E+29  -5.057  10148. ! mtbe017d.mec avg err
14.66%
CC.CQ + O2      <=> CCQCQ.          1.05E+13  -1.019  10546. ! mtbe017d.mec avg err  9.65%
CC.CQ + O2      <=> C*CQC + HO2B     3.46E+51 -12.618  16169. ! mtbe017d.mec avg err
31.22%
CC.CQ + O2      <=> C2.CQ + O2       1.35E+38  -8.463  21716. ! mtbe017d.mec avg err 28.18%
CC*C + OH       <=> C2.COH          2.32E+43  -9.486  21511. ! mtbe017d.mec avg err 29.93%
CC*C + OH       <=> C*COH + CH3      2.32E+45 -10.440   9210. ! mtbe017d.mec avg err
18.59%
CC*C + OH       <=> C*COHC + H       2.22E+21  -2.819   7968. ! mtbe017d.mec avg err 10.07%
CC*C + OH       <=> C2C.OH          1.79E+19  -2.136   8591. ! mtbe017d.mec avg err  7.47%
CC*C + OH       <=> C2C*O + H        1.58E+35  -7.376  15737. ! mtbe017d.mec avg err 15.83%
CC*C + OH       <=> C2CO.           1.90E+19  -1.876  14921. ! mtbe017d.mec avg err 17.77%
CC*C + OH       <=> CH3CHO + CH3     1.97E+08   -.353  11785. ! mtbe017d.mec avg err
19.65%
C2.COH        <=> C*COH + CH3       9.80E+08   .952  14107. ! mtbe017d.mec avg err  3.26%
C2.COH        <=> C*COHC + H       1.93E+44 -10.506  36701. ! mtbe017d.mec avg err 18.38%
C2.COH        <=> C2C.OH          7.57E+43 -10.357  38908. ! mtbe017d.mec avg err 18.47%
C2.COH        <=> C2C*O + H        3.36E+53 -13.561  45427. ! mtbe017d.mec avg err 24.14%
C2.COH        <=> C2CO.           5.15E+39  -8.885  44835. ! mtbe017d.mec avg err 16.71%
C2.COH        <=> CH3CHO + CH3     2.64E+28  -7.281  42376. ! mtbe017d.mec avg err
40.84%
C2C.OH        <=> C*COHC + H       3.70E+29  -6.182  44633. ! mtbe017d.mec avg err 25.63%
C2C.OH        <=> C2C*O + H        1.58E+56 -14.024  51486. ! mtbe017d.mec avg err 29.30%
C2CO.         <=> C2C.OH          1.02E+42  -9.439  36732. ! mtbe017d.mec avg err 45.34%
C2CO.         <=> CH3CHO + CH3     1.53E+37 -10.648  13935. ! mtbe017d.mec avg err 22.97%
C2CO.         <=> C2C*O + H        3.40E+39  -9.287  16735. ! mtbe017d.mec avg err 12.05%
C2.COH + O2     <=> CCOHCQ.          5.99E+37  -9.066  18453. ! mtbe017d.mec avg err 13.00%
C2.COH + O2     <=> C*COHCB + HO2B    8.99E+35  -7.908   6030. ! mtbe017d.mec avg err
9.15%
C2.COH + O2     <=> CCO.CQ          7.05E+20  -2.769   8604. ! mtbe017d.mec avg err 17.44%
C2.COH + O2     <=> CQCHO + CH3      3.65E+26  -5.989   6571. ! mtbe017d.mec avg err
13.44%
C2.COH + O2     <=> CH3CHO + CH2OOH   9.94E+21  -3.479   9807 ! mtbe017d.mec avg err
13.42%
C2.COH + O2     <=> CC*OCQ + H       5.18E+22  -3.508   9783. ! mtbe017d.mec avg err
13.46%
C2.COH + O2     <=> CCOHC.Q         1.98E+18  -2.663  10805. ! mtbe017d.mec avg err 11.92%
C2.COH + O2     <=> CC*CQ + OH       1.83E+09   -.331  16000. ! mtbe017d.mec avg err  8.33%
C2.COH + O2     <=> CCOHCHO + OH     1.40E-11   6.161  18369. ! mtbe017d.mec avg err
8.77%
C2.COH + O2     <=> C.COHCQ         1.92E+12   -.087  16733. ! mtbe017d.mec avg err  4.66%
C2.COH + O2     <=> C*COH + CH2OOH    6.40E+33  -7.003  10967. ! mtbe017d.mec avg err
32.90%
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```
C2.COH + O2      <=> C*CCQ + OH        1.23E+28  -4.928  21593. ! mtbe017d.mec avg err
20.31%
C2.COH + O2      <=> OHCYCCOC + OH     1.69E+29  -4.837  22410. ! mtbe017d.mec avg err
18.92%
C2.COH + O2      <=> CC.OHCQ           7.64E+31  -6.241  16227 ! mtbe017d.mec avg err 31.54%
C2.COH + O2      <=> YCOCICOH + OH     2.44E+37  -7.939  10915. ! mtbe017d.mec avg err
14.06%
CCOHCQ.          <=> C*COHCB + HO2B    4.62E+31  -5.741  14844. ! mtbe017d.mec avg err
24.86%
CCOHCQ.          <=> CCO.CQ            4.58E+34  -7.334  32364. ! mtbe017d.mec avg err  8.13%
CCOHCQ.          <=> CQCHO + CH3       3.50E+53 -14.046  35099. ! mtbe017d.mec avg err
12.40%
CCOHCQ.          <=> CH3CHO + CH2OOH   1.73E+44 -10.412  39083. ! mtbe017d.mec avg err
9.96%
CCOHCQ.          <=> CC*OCQ + H        9.59E+44 -10.448  39029. ! mtbe017d.mec avg err
9.90%
CCOHCQ.          <=> CCOHC.Q           4.20E+39  -9.349  40913. ! mtbe017d.mec avg err 12.30%
CCOHCQ.          <=> CC*CQ + OH        9.35E+25  -5.749  46688. ! mtbe017d.mec avg err
14.42%
CCOHCQ.          <=> CCOHCHO + OH      4.25E+00   2.107  47260. ! mtbe017d.mec avg err
19.83%
CCOHCQ.          <=> C.COHCQ           8.19E+28  -5.496  47353. ! mtbe017d.mec avg err 20.85%
CCOHCQ.          <=> C*COH + CH2OOH    1.03E+41  -9.443  30739. ! mtbe017d.mec avg err
17.41%
CCOHCQ.          <=> C*CCQ + OH        2.01E+40  -8.917  50620. ! mtbe017d.mec avg err  6.76%
CCOHCQ.          <=> OHCYCCOC + OH     1.84E+41  -8.781  51573. ! mtbe017d.mec avg err
7.25%
CCOHCQ.          <=> CC.OHCQ           1.78E+42  -9.652  41508. ! mtbe017d.mec avg err 11.95
CCOHCQ.          <=> YCOCICOH + OH     2.21E+44 -10.290  29359. ! mtbe017d.mec avg err
23.87%
CCO.CQ           <=> CQCHO + CH3       4.13E+45 -10.268  40328. ! mtbe017d.mec avg err
24.24%
CCO.CQ           <=> CH3CHO + CH2OOH   7.27E+24  -4.731  13001. ! mtbe017d.mec avg err
20.07%
CCO.CQ           <=> CC*OCQ + H        5.56E+25  -4.810  12993. ! mtbe017d.mec avg err 20.48%
CCO.CQ           <=> CCOHC.Q           1.72E+19  -3.286  15067. ! mtbe017d.mec avg err 13.40%
CCO.CQ           <=> CCOHCHO + OH      9.79E+17  -4.392  29263. ! mtbe017d.mec avg err
7.12%
CCO.CQ           <=> C.COHCQ           7.24E+20  -4.112  29916. ! mtbe017d.mec avg err  1.66%
CCO.CQ           <=> OHCYCCOC + OH     1.60E+47 -12.268  21280. ! mtbe017d.mec avg err
27.74%
CCO.CQ           <=> CC.OHCQ           1.23E+38  -9.484  25742. ! mtbe017d.mec avg err 28.61%
CCO.CQ           <=> YCOCICOH + OH     2.12E+54 -14.187  22594. ! mtbe017d.mec avg err
30.34%
CCOHC.Q          <=> CC*CQ + OH        1.67E+43 -10.603  25698. ! mtbe017d.mec avg err
30.61%
CCOHC.Q          <=> CCOHCHO + OH      6.73E+68 -21.018  46584. ! mtbe017d.mec avg err
33.10%
CCOHC.Q          <=> C.COHCQ           4.31E+35  -8.320   8272. ! mtbe017d.mec avg err 75.53%
CCOHC.Q          <=> CC.OHCQ           2.48E+19  -6.863   4568. ! mtbe017d.mec avg err 81.83%
CCOHC.Q          <=> YCOCICOH + OH     2.80E+19  -6.779   3678. ! mtbe017d.mec avg err
57.92%
C.COHCQ          <=> CCOHCHO + OH      4.64E+50 -15.756  30683. ! mtbe017d.mec avg err
74.63%
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```
C.COHCQ        <=> C*COH + CH2OOH     2.44E+30  -6.260  37465. ! mtbe017d.mec avg err
12.03%
C.COHCQ        <=> C*CCQ + OH         2.30E+25  -4.469  31175. ! mtbe017d.mec avg err
15.06%
C.COHCQ        <=> OHCYCCOC + OH      7.90E+26  -4.487  32461. ! mtbe017d.mec avg err
14.25%
C.COHCQ        <=> CC.OHCQ            7.42E+23  -4.364  19295. ! mtbe017d.mec avg err 18.15%
C.COHCQ        <=> YCOCICOH + OH      9.97E+43 -10.426  24327. ! mtbe017d.mec avg err
44.39%
CC.OHCQ        <=> YCOCICOH + OH      1.44E+45 -10.380  32432. ! mtbe017d.mec avg err
48.39%
CC*C + OH      <=> CC.COH             9.87E+26  -4.957  24388. ! mtbe017d.mec avg err  8.99%
CC*C + OH      <=> C*CCOH + H         8.15E+45 -10.627   8794. ! mtbe017d.mec avg err
19.54%
CC*C + OH      <=> CC*COH + H         2.40E+15   -.913  13166. ! mtbe017d.mec avg err  2.20%
CC*C + OH      <=> CCCO.              7.05E+16  -1.465   9003. ! mtbe017d.mec avg err  5.91%
CC*C + OH      <=> C2H5 + HCHO        9.27E+08   -.423  14783. ! mtbe017d.mec avg err
17.64%
CC*C + OH      <=> CCC*O + H          3.53E+08   1.064  16918. ! mtbe017d.mec avg err  1.35%
CC*C + OH      <=> CCC.OH             8.92E+04   1.995  16473. ! mtbe017d.mec avg err  1.38%
CC*C + OH      <=> C.CCOH             1.83E+38  -8.366  17897. ! mtbe017d.mec avg err 17.27%
CC*C + OH      <=> C2H4 + CH2OH       7.72E+30  -5.889  21275. ! mtbe017d.mec avg err
13.15%
CC.COH         <=> C*CCOH + H         3.50E+14   -.314  20485. ! mtbe017d.mec avg err 16.36%
CC.COH         <=> CC*COH + H         6.71E+35  -8.050  42929. ! mtbe017d.mec avg err 21.12%
CC.COH         <=> CCCO.              5.29E+40  -9.559  39078. ! mtbe017d.mec avg err 18.77%
CC.COH         <=> C2H5 + HCHO        3.87E+26  -6.692  44207. ! mtbe017d.mec avg err 38.41%
CC.COH         <=> CCC*O + H          3.34E+26  -5.371  46266. ! mtbe017d.mec avg err 20.78%
CC.COH         <=> CCC.OH             5.18E+22  -4.403  45657. ! mtbe017d.mec avg err 21.22%
CC.COH         <=> C.CCOH             1.43E+55 -14.203  46908. ! mtbe017d.mec avg err 25.79%
CCCO.          <=> C2H5 + HCHO        1.19E+46 -11.363  50074. ! mtbe017d.mec avg err 26.70%
CCCO.          <=> CCC*O + H          5.33E+40  -9.622  17781. ! mtbe017d.mec avg err  9.83%
CCCO.          <=> CCC.OH             3.22E+40  -9.711  22835. ! mtbe017d.mec avg err 13.48%
CCCO.          <=> C*COH + CH3        1.18E+39 -11.298  15162. ! mtbe017d.mec avg err 19.42%
CCCO.          <=> CC*COH + H         1.67E+36 -10.045  27654. ! mtbe017d.mec avg err 30.37%
CCCO.          <=> C.CCOH             2.85E+42 -12.132  33555. ! mtbe017d.mec avg err 23.04%
CCCO.          <=> C2H4 + CH2OH       3.89E+36 -10.615  14400. ! mtbe017d.mec avg err 23.02%
CCC.OH         <=> C*COH + CH3        3.85E+38 -10.808  29442. ! mtbe017d.mec avg err
25.94%
CCC.OH         <=> CCC*O + H          6.32E+40  -9.095  38006. ! mtbe017d.mec avg err 17.83%
CCC.OH         <=> CC*COH + H         1.21E+41  -8.993  36744. ! mtbe017d.mec avg err 19.39%
CCC.OH         <=> C.CCOH             2.15E+40  -9.066  42009. ! mtbe017d.mec avg err 15.41%
C.CCOH         <=> C2H4 + CH2OH       2.83E+40  -9.876  54645. ! mtbe017d.mec avg err
32.15%
C.CCOH         <=> C*CCOH + H         1.71E+47 -11.209  35915. ! mtbe017d.mec avg err 45.78%
CC.COH + O2      <=> CCQ.COH          4.39E+59 -15.421  47955. ! mtbe017d.mec avg err
24.72%
CC.COH + O2      <=> CC*COHB + HO2B   5.30E+44 -10.597   8232. ! mtbe017d.mec avg err
17.52%
CC.COH + O2      <=> C*CCOHB + HO2B   8.98E+23  -3.583   9058. ! mtbe017d.mec avg err
13.56%
CC.COH + O2      <=> CCQCO.           1.07E+17  -1.635   9957. ! mtbe017d.mec avg err  8.16%
CC.COH + O2      <=> CC.Q + HCHO      2.06E+34  -8.092   9128. ! mtbe017d.mec avg err
12.85%
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CC.COH + O2      <=> CCQC.OH          1.01E+29  -5.439  11391. ! mtbe017d.mec avg err
13.30%
CC.COH + O2      <=> CC*COH + HO2     1.50E+44 -10.243  11864. ! mtbe017d.mec avg err
12.29%
CC.COH + O2      <=> C.CQCOH          3.39E+33  -6.279  14042. ! mtbe017d.mec avg err
16.15%
CC.COH + O2      <=> C*CCOH + HO2     8.48E+35  -8.039  10741. ! mtbe017d.mec avg err
16.04%
CC.COH + O2      <=> C*CQ + CH2OH     2.93E+29  -5.222  13392. ! mtbe017d.mec avg err
15.38%
CC.COH + O2      <=> CC.QCOH          1.92E+13   -.756  17747. ! mtbe017d.mec avg err  4.63%
CC.COH + O2      <=> CC*OCOH + OH     1.47E+10   -.680  13564. ! mtbe017d.mec avg err
2.18%
CCQ.COH        <=> CC*COHB + HO2B     2.76E+12   -.348  14110. ! mtbe017d.mec avg err
3.83%
CCQ.COH        <=> C*CCOHB + HO2B     2.80E+42  -9.594  35727. ! mtbe017d.mec avg err
16.01%
CCQ.COH        <=> CCQCO.           6.36E+39  -8.951  40988. ! mtbe017d.mec avg err 19.67%
CCQ.COH        <=> CC.Q + HCHO      1.31E+52 -13.481  35098. ! mtbe017d.mec avg err
24.42%
CCQ.COH        <=> CCQC.OH          1.58E+53 -12.997  42526. ! mtbe017d.mec avg err 14.16%
CCQ.COH        <=> CC*COH + HO2     1.65E+51 -12.481  32321. ! mtbe017d.mec avg err
30.23%
CCQ.COH        <=> C.CQCOH          2.53E+53 -12.605  43281. ! mtbe017d.mec avg err 21.93%
CCQ.COH        <=> C*CCOH + HO2     1.68E+55 -13.916  39680. ! mtbe017d.mec avg err
13.08%
CCQ.COH        <=> C*CQ + CH2OH     5.53E+52 -12.572  44482. ! mtbe017d.mec avg err
22.43%
CCQ.COH        <=> CC.QCOH          5.92E+30  -6.584  49173. ! mtbe017d.mec avg err 30.60%
CCQ.COH        <=> CC*OCOH + OH     3.62E+29  -7.044  45193. ! mtbe017d.mec avg err
24.08%
CCQCO.         <=> CC.Q + HCHO      5.61E+31  -6.701  45672. ! mtbe017d.mec avg err 29.24%
CCQCO.         <=> CCQC.OH          1.59E+25  -4.595  13737. ! mtbe017d.mec avg err 14.91%
CCQCO.         <=> CC*COH + HO2     1.79E+56 -14.717  23771. ! mtbe017d.mec avg err
44.03%
CCQCO.         <=> C.CQCOH          4.79E+48 -11.991  28062. ! mtbe017d.mec avg err 26.00%
CCQCO.         <=> C*CCOH + HO2     4.01E+53 -14.264  25951. ! mtbe017d.mec avg err
24.84%
CCQCO.         <=> C*CQ + CH2OH     4.45E+46 -11.553  28502. ! mtbe017d.mec avg err
20.13%
CCQCO.         <=> CC.QCOH          1.10E+22  -4.719  31585. ! mtbe017d.mec avg err  6.78%
CCQCO.         <=> CC*OCOH + OH     6.05E+20  -5.177  27703. ! mtbe017d.mec avg err
2.45%
CCQC.OH        <=> CC.Q + HCHO      8.40E+22  -4.815  28178. ! mtbe017d.mec avg err
6.38%
CCQC.OH        <=> CC*COH + HO2     8.41E+51 -12.792  37704. ! mtbe017d.mec avg err
13.09%
CCQC.OH        <=> C.CQCOH          1.51E+31  -6.146  25501. ! mtbe017d.mec avg err  5.35%
CCQC.OH        <=> C*CCOH + HO2     2.70E+55 -14.166  35936. ! mtbe017d.mec avg err
17.02%
CCQC.OH        <=> C*CQ + CH2OH     1.84E+52 -12.595  39851. ! mtbe017d.mec avg err
18.29%
CCQC.OH        <=> CC.QCOH          5.81E+28  -6.189  42500. ! mtbe017d.mec avg err 23.96%
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```
CCQC.OH          <=> CC*OCOH + OH      5.03E+27  -6.685  38825. ! mtbe017d.mec avg err
16.83%
C.CQCOH          <=> CC.Q + HCHO       8.34E+29  -6.350  39315. ! mtbe017d.mec avg err
21.76%
C.CQCOH          <=> CC*COH + HO2      1.32E+44 -10.919  30945. ! mtbe017d.mec avg err
17.63%
C.CQCOH          <=> C*CCOH + HO2      6.35E+46 -11.229  32912. ! mtbe017d.mec avg err
19.66%
C.CQCOH          <=> C*CQ + CH2OH      2.64E+30  -6.150  18383. ! mtbe017d.mec avg err
20.92%
C.CQCOH          <=> CC.QCOH           7.67E+16  -2.315  29967. ! mtbe017d.mec avg err 22.02%
C.CQCOH          <=> CC*OCOH + OH      5.47E-19   5.742  -1293. ! mtbe017d.mec avg err
97.54%
CC.QCOH          <=> CC.Q + HCHO       2.91E-18   6.537  -1073. ! mtbe017d.mec avg err
100.24%
CC.QCOH          <=> CC*COH + HO2      1.03E-04   2.211  17690. ! mtbe017d.mec avg err
76.89%
CC.QCOH          <=> C*CCOH + HO2      3.45E-23   8.257  13151. ! mtbe017d.mec avg err
30.36%
CC.QCOH          <=> C*CQ + CH2OH      7.44E+46 -12.367  30557. ! mtbe017d.mec avg err
52.77%
CC.QCOH          <=> CC*OCOH + OH      2.30E-05   3.094  42001. ! mtbe017d.mec avg err
.87%
YCOCICQ          <=> CCYC.OC + HO2     2.41E+09   -.098   -482. ! mtbe017d.mec avg err
1.83%
YCOCICOH         <=> CCYC.OC + OH      5.98E+43  -8.499  82399. ! mtbe017d.mec avg err
63.10%
CC.C*O + HO2     <=> CCQCHO            2.53E+33  -5.179 102022. ! mtbe017d.mec avg err
53.01%
CC.C*O + HO2     <=> CHO + CC.Q        2.17E+43 -10.080   7311. ! mtbe017d.mec avg err
19.20%
CC.C*O + HO2     <=> CCQC.*O + H       1.66E+02   3.302  15057. ! mtbe017d.mec avg err
9.49%
CC.C*O + HO2     <=> CCO.C*O + OH      8.18E+00   3.294  26639. ! mtbe017d.mec avg err
93.22%
CCQCHO           <=> CHO + CC.Q        2.38E+18  -1.480   4596. ! mtbe017d.mec avg err  6.90%
CCQCHO           <=> CCQC.*O + H       1.01E+40  -8.249  81687. ! mtbe017d.mec avg err
21.19%
CCQCHO           <=> CCO.C*O + OH      3.40E+34  -7.180  91354. ! mtbe017d.mec avg err
21.18%
CC.C*O + OH      <=> CCOHCHO           8.19E+45  -9.881  52692. ! mtbe017d.mec avg err
35.68%
CC.C*O + OH      <=> CHO + CC.OH       6.28E+42  -9.304   9517. ! mtbe017d.mec avg err
56.35%
CC.C*O + OH      <=> CCOHC.*O + H      1.61E+12    .587   6765. ! mtbe017d.mec avg err
46.76%
CCOHCHO          <=> CHO + CC.OH       8.55E+06   1.488   9994. ! mtbe017d.mec avg err
37.11%
CCOHCHO          <=> CCOHC.*O + H      6.26E+38  -7.084  84212. ! mtbe017d.mec avg err
54.54%
CCOHC.*O         <=> CC.OH + CO        2.67E+46  -9.993  98371. ! mtbe017d.mec avg err
50.94%
CCQC.*O          <=> CC.Q + CO         4.50E+21  -3.762   9473. ! mtbe017d.mec avg err 25.66%
```

```
CC*OCQ          <=> CC*OCO. + OH       2.39E-21  -3.602  10018. ! mtbe017d.mec avg err
23.25%
CC*OCO.         <=> CC*OC*O + H        2.61E-47 -10.310  53941. ! mtbe017d.mec avg err
38.00%
CC*OCO.         <=> CH3C.*O + HCHO     1.51E+10   -.488  19749. ! mtbe017d.mec avg err
12.06%
C*CC.*O         <=> CO + C2H3          2.58E+16  -2.300   5113. ! mtbe017d.mec avg err 22.87%
END
```

APPENDIX IIB

TRANSITION STATES IN THE MTBE SYSTEM

TS IIB. 1 Thermodynamic Properties from MOPAC PM3

SPECIES	$H_{f,298}$[a]	S_{298}[b]	C_p[b] 300	400	500	600	800	1000	1500	DATE		ELEMENTS				
HO2	3.5	54.73	8.37	8.95	9.48	9.96	10.78	11.43	12.47	JANAF	H	1	O	2	0	0 G 0
C3CQ.	-23.58	83.36	29.46	36.78	43.1	48.24	55.85	61.25	69.59	3/5/97 CHEN	C	4	H	9	O	2 0 G 4
C3.CQ	-10.68	92.19	31.31	38.68	44.91	49.9	57.1	62.04	69.54	3/5/97 CHEN	C	4	H	9	O	2 0 G 5
C2C*C	-3.8	71.01	20.4	25.42	30.16	34.27	40.89	45.92	53.96	3/5/97 CHEN	C	4	H	8		0 0 G 2
C2C.CQ	-9.29	97.76	29.21	35.75	41.77	46.86	54.58	60.07	68.48	3/5/97 CHEN	C	4	H	9	O	2 0 G 5
C2CCQ.	-17.59	89.44	28.69	36.06	42.43	47.59	55.3	60.85	69.41	3/5/97 CHEN	C	4	H	9	O	2 0 G 4
C2.CCQ	-4.69	96.38	31.24	38.51	44.72	49.68	56.86	61.85	69.47	3/5/97 CHEN	C	4	H	9	O	2 0 G 5
C*CICCQ.	11.72	89.74	26.09	31.72	36.75	41	47.61	52.49	60.03	3/5/97 CHEN	C	4	H	7	O	2 0 G 3
C*CICC.Q	9.12	90.11	29.59	35.34	40.24	44.25	50.26	54.53	61.08	3/5/97 CHEN	C	4	H	7	O	2 0 G 4
C*CIC.CQ	11.72	91.2	28.79	35.05	40.28	44.47	50.58	54.83	61.27	3/5/97 CHEN	C	4	H	7	O	2 0 G 4
C2.CYCOOC	27.81	83.74	25.49	32.34	38.12	42.75	49.53	54.29	61.51	3/5/97 CHEN	C	4	H	7	O	2 0 G 2
CCYC.COOC	9.84	81.75	25.27	32.01	37.8	42.51	49.59	54.63	62.22	3/5/97 CHEN	C	4	H	7	O	2 0 G 1
C2COHCQ.	-60.19	96.02	32.85	40.56	47.2	52.53	60.33	65.8	74.22	3/5/97 CHEN	C	4	H	9	O	3 0 G 5
C2CO.CQ	-44.33	96.6	33.58	41.37	47.9	53.09	60.55	62.65	73.37	3/5/97 CHEN	C	4	H	9	O	3 0 G 5
C2CQ.COH	-59.38	96.14	33.23	40.71	47.14	52.34	60.06	65.55	74.06	3/5/97 CHEN	C	4	H	9	O	3 0 G 5
C2CQCO.	-43.52	95.17	34.49	42.65	49.6	55.14	62.98	68.18	75.8	3/5/97 CHEN	C	4	H	9	O	3 0 G 5
C2.COHCQ	-47.29	100.36	34.66	42.21	48.5	53.47	60.69	65.74	73.58	3/5/97 CHEN	C	4	H	9	O	3 0 G 6
C2.CQCOH	-46.48	103.99	35.12	42.76	49.13	54.19	61.48	66.47	74.1	3/5/97 CHEN	C	4	H	9	O	3 0 G 6
C2CQC.OH	-53.58	100.1	35.47	42.78	49.03	54.07	61.39	66.4	74.06	3/5/97 CHEN	C	4	H	9	O	3 0 G 6
C2CQ.CQ	-47.67	102.62	37.48	46.11	53.21	58.78	66.65	71.99	80	3/5/97 CHEN	C	4	H	9	O	4 0 G 6
C2.CQCQ	-31.87	110.04	39.69	48.06	54.91	60.23	67.67	72.58	79.82	3/5/97 CHEN	C	4	H	9	O	4 0 G 7
C2CQCQ.	-44.77	102.68	37.34	46.06	53.34	59.06	67.13	72.5	80.39	3/5/97 CHEN	C	4	H	9	O	4 0 G 6
C2CQC.Q	-36.97	106.93	39.56	47.96	54.96	60.47	68.14	73.07	80.21	3/5/97 CHEN	C	4	H	9	O	4 0 G 7
TC2YCQC	29.53	82.05	28.92	36.75	43.38	48.7	56.48	61.9	70.09	3/5/97 CHEN	C	4	H	9	O	2 0 G 2
TC2YCXQC*	30.39	84.54	29.77	37.14	43.47	48.64	56.32	61.75	70.01	3/5/97 CHEN	C	4	H	9	O	2 0 G 2
TC3*CXQ	20.52	90.91	29.9	36.85	42.79	47.62	54.79	59.88	67.82	3/5/97 CHEN	C	4	H	9	O	2 0 G 4
TC2YC2OXP	11.1	86.99	29.19	36.43	42.6	47.53	54.8	59.99	68.19	3/5/97 CHEN	C	4	H	9	O	2 0 G 3
TC2CJ*CXQ	15.53	91.28	29.1	36.11	42.18	47.12	54.47	59.68	67.74	3/5/97 CHEN	C	4	H	9	O	2 0 G 4
TC2YCCOXP	4.45	87.97	29.11	36.18	42.32	47.29	54.67	59.95	68.24	3/5/97 CHEN	C	4	H	9	O	2 0 G 3
TC2YCCQ	25.61	83.17	28.67	36.47	43.18	48.58	56.49	61.98	70.21	3/5/97 CHEN	C	4	H	9	O	2 0 G 2

Table IIB. 1 Thermodynamic Properties from MOPAC PM3 (Cont')

SPECIES	$H_{f,298}$[a]	S_{298}[b]	C_p[b] 300	400	500	600	800	1000	1500	DATE		ELEMENTS					
TC2YC*CXQ	32.54	82.61	27.82	35.05	41.42	46.73	54.8	60.59	69.39	3/5/97	CHEN C	4	H	9	O	2	0 G 2
TCYCCQC	21.11	80.34	27.09	35.27	42.3	47.97	56.31	62.12	70.77	3/5/97	CHEN C	4	H	9	O	2	0 G 1
TC2*CYCQ	55.09	86.82	26.65	32.85	38.08	42.34	48.72	53.28	60.16	3/5/97	CHEN C	4	H	7	O	2	0 G 2
TC*YCCQC	47.97	79.76	25.33	32.43	38.31	43.02	49.94	54.76	61.92	3/5/97	CHEN C	4	H	7	O	2	0 G 0
TC2*YCOOC	51.07	82.17	25.24	31.31	36.61	41.01	47.73	52.61	60.12	3/5/97	CHEN C	4	H	7	O	2	0 G 1
TCYC*COOC	50.37	79.36	24.59	30.89	36.34	40.84	47.67	52.6	60.15	3/5/97	CHEN C	4	H	7	O	2	0 G 1
TC*YC3OXP	37.45	84.33	25.52	32.02	37.4	41.71	48.12	52.74	59.96	3/5/97	CHEN C	4	H	7	O	2	0 G 1
TC2YCCQO	-15.29	84.3	30.26	38.86	46.23	52.17	60.82	66.77	75.57	3/5/97	RU C	4	H	9	O	3	0 G 2
TICPYCCQC	-19.64	85.37	30.94	39.46	46.65	52.39	60.75	66.53	75.23	3/5/97	RU C	4	H	9	O	3	0 G 2
TC2YCQOC	-15.13	84.71	30.51	39.07	46.39	52.29	60.9	66.83	75.61	3/5/97	CHEN C	4	H	9	O	3	0 G 2
TICCPYCQC	-8.76	91.89	32.04	40.16	46.96	52.41	60.4	66	74.47	3/5/97	CHEN C	4	H	9	O	3	0 G 3
TC2YCQCIP	-12.27	89.51	32.7	40.83	47.69	53.15	61.06	66.52	74.75	3/5/97	CHEN C	4	H	9	O	3	0 G 3
TICCQYCQC	7.89	101	37.38	46.46	53.93	59.75	67.84	73.15	80.85	3/5/97	CHEN C	4	H	9	O	4	0 G 4
TC2YCQOOC	5.87	86.09	30.51	39.07	46.39	52.29	60.9	66.83	75.61	3/5/97	CHEN C	4	H	9	O	4	0 G 2
TC2YCQCIQ	4.95	98.22	37.71	46.64	54.04	59.84	67.94	73.23	80.89	3/5/97	CHEN C	4	H	9	O	4	0 G 4
TICQYCCQC	0.66	95.34	36.07	45.32	53.02	59.09	67.68	73.35	81.46	3/5/97	CHEN C	4	H	9	O	4	0 G 3
C2COHC.Q	-52.39	103.01	35.65	42.94	49.05	53.92	61.03	65.99	73.74	3/5/97	RU C	4	H	9	O	3	0 G 6
TC2CPYCQ	-13.31	92.02	33.7	41.48	48	53.16	60.66	65.89	73.91	3/5/97	RU C	4	H	9	O	3	0 G 4
TICCQYCPC	-9.9	92.5	33.73	42.11	49.09	54.59	62.33	67.47	74.99	3/5/97	RU C	4	H	9	O	3	0 G 4
TC2YCPCIQ	-16.13	88.69	33.14	41.26	48.17	53.68	61.59	66.93	74.72	3/5/97	RU C	4	H	9	O	3	0 G 4
TICPYC3OXP	-33.53	90.95	32.03	39.64	46.08	51.27	58.96	64.48	73.21	3/5/97	RU C	4	H	9	O	3	0 G 3
C3COC	-68.9	85.64	32.85	41.42	48.89	55.01	64.39	71.31	82.33	3/5/97	RU C	5	H	12	O	1	0 G 5
CH3OH	-48	57.26	10.8	12.63	14.59	16.33	19.17	21.38	25.04	3/5/97	RU C	1	H	4	O	1	0 G 1
TMTBE	-1.3	86.37	33	41.72	49.23	55.41	64.9	71.86	82.77	3/29/97	RU C	5	H	12	O	1	0 G 2
TMEOH	45.06	54.87	10.62	12.89	15.05	16.94	19.96	22.18	25.49	3/29/97	RU C	1	H	4	O	1	0 G 0
C3C.	11.9	75.1	22.54	27.44	32.28	36.61	43.65	49.08	57.83	3/5/96	CHEN C	4	H	9		0	0 G 3
TC2CJ*CXH	49.15	74.35	22.87	28.38	33.35	37.63	44.46	49.61	57.79	3/5/96	CHEN C	4	H	9		0	0 G 2
C2CY2CO	-24.81	72.63	22.98	29.75	35.67	40.5	47.68	52.78	60.58	3/5/96	CHEN C	4	H	9	O	1	0 G 2
TCYCOOH	39.3	71.46	18.1	22.3	25.83	27.73	31.32	34.52	39.29	3/30/96	BOZZ C	2	H	5	O	2	0 G 1
TYCCOOH	29.6	70.94	17.44	21.97	25.84	28.96	33.54	36.72	41.41	3/30/96	BOZZ C	2	H	5	O	2	0 G 0

Table IIB. 1 Thermodynamic Properties from MOPAC PM3 (Cont')

SPECIES	$H_{f,298}$[a]	S_{298}[b]	C_p[b] 300	400	500	600	800	1000	1500	DATE		ELEMENTS					
TCYCOCXOH	32	73.59	17.72	21.69	25.06	27.78	31.82	34.77	39.48	3/30/96 BOZZ	C	2 H	5 O	2 0 G	1		
TCQJCQ	1.2	87.57	25.81	31.07	35.48	38.98	43.93	47.19	51.71	3/30/96 BOZZ	C	2 H	5 O	4 0 G	2		
TIPRXOOH	19	83.21	24.53	29.11	33.24	36.75	42.32	46.51	53.31	3/30/96 BOZZ	C	3 H	7 O	2 0 G	2		
TIPROXOH	18	78.11	23.31	28.69	33.04	36.97	42.82	46.83	53.51	3/30/96 BOZZ	C	3 H	7 O	2 0 G	2		
TIPRYQE	18.2	76.86	23.63	29.2	34.02	38.01	44.13	48.55	55.28	3/30/96 BOZZ	C	3 H	7 O	2 0 G	1		
TIPROOXH	18.2	75.82	23.09	29.03	34.09	38.23	44.4	48.81	55	3/30/96 BOZZ	C	3 H	7 O	2 0 G	1		
TC*YCOOJ	54.89	67.46	15.06	18.16	20.74	22.8	25.84	28	31.26	3/30/96 BOZZ	C	2 H	3 O	2 0 G	0		
TYC*COOH	62.23	67.67	15.09	18.64	21.4	23.7	26.85	28.95	31.93	3/30/96 BOZZ	C	2 H	3 O	2 0 G	0		
TYVOOH	68	69.4	16.1	19.22	21.71	23.71	26.66	28.71	31.73	3/30/96 BOZZ	C	2 H	3 O	2 0 G	0		
TC*CXO2	71.6	76.1	16.33	18.7	20.68	22.31	24.92	26.91	30.13	3/30/96 BOZZ	C	2 H	3 O	2 0 G	0		
TYVOOHS	66.3	67.96	15.75	19.21	22.09	24.24	27.26	29.26	31.1	3/30/96 BOZZ	C	2 H	3 O	2 0 G	0		
TC*COXO	62.72	68.4	15.81	18.64	21.01	22.94	25.86	28.82	31.23	3/30/96 BOZZ	C	2 H	3 O	2 0 G	0		
H	52.1	27.3	4.9	4.9	4.9	4.9	4.9	4.9	4.9		H	1	0	0 0 G	0		

a Unit in kcal-mol^{-1}.
b Unit in cal-mol^{-1}-K^{-1}

TS IIB. 2 TS Information for MTBE → C2C=C + CH_3OH

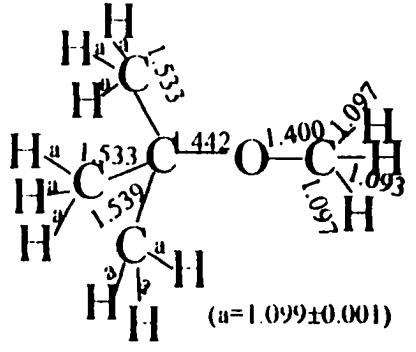
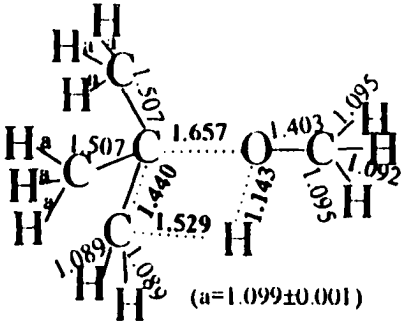
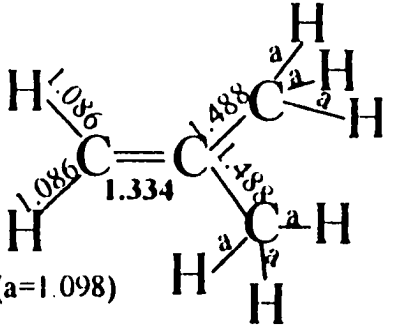
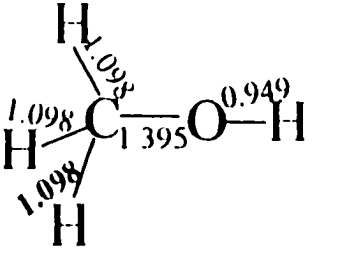
Reactant	Transition State	Product 1	Product 2
 (a=1.099±0.001)	 (a=1.099±0.001)	 (a=1.098)	
C3COC (MTBE)	TSMTBE	C2C=C	CH_3OH
Principle moments of inertia in unit of cm^{-1}: A = 0.145357 B = 0.091250 C = 0.090246 in unit of 10^{-40}-gram-cm^2: A = 192.578843 B = 306.770121 C = 310.182958	Principle moments of inertia in unit of cm^{-1}: A = 0.139810 B = 0.087818 C = 0.085587 in unit of 10^{-40}-gram-cm^2: A = 200.219214 B = 318.758215 C = 327.067124	Principle moments of inertia in unit of cm^{-1}: A = 0.312646 B = 0.278927 C = 0.156031 in unit of 10^{-40}-gram-cm^2: A = 89.534710 B = 100.358468 C = 179.404128	Principle moments of inertia in unit of cm^{-1}. A = 4.244786 B = 0.856787 C = 0.825179 in unit of 10^{-40}-gram-cm^2. A = 6.594594 B = 32.671649 C = 33.923121
Symmetry = 243	Symmetry = 9	Symmetry = 18	Symmetry = 3
Internal rotor(s): V / kcal-mol^{-1} CH_3-C(C2)OH (3): 4.01 C3C-OCH_3 (1): 3.0 C3CO-CH_3 (1): 2.0	Internal rotor(s): V / kcal-mol^{-1} CH_3-C(C2)OH (2): 4.01 TC2yCCHO-CH_3 (1): 2.0	Internal rotor(s). V / kcal-mol^{-1} CH_3-C_2H_3(C) (2): 1.26	Internal rotor(s): V / kcal-mol^{-1} CH_3-OH (1): 1.09
-147.13 -50.78 132.26 166.25	-1507.06 9.81 85.42 131.81	-116 108 393 423 471 618 932	292.33 988 92 1020.76 1164.45

Table IIB. 2 TS Information for MTBE → C2C=C + CH3OH (Cont')

Reactant	Transition State	Product 1	Product 2
174.70 263.64 354 18 384.01	156.12 232.38 289.03 371.28	937 943 985 993 1024 1069	1362 29 1366 05 1366.27
433.99 494.67 570.33	421.06 476.74 506.60 554.17	1312 1323 1382 1390 1397	1409.05 3035 71 3068.61
847.04767 907.40 947.78	595.25 863.31 934.90 939.70	1398 1399 1477 1873 3073	3141 15 3896 48
962.81 976 05 1008.28 1014.88	955.48 974.38 981.57 987 02	3074 3074 3077 3147 3148	
1016.87 1093.17 1165.37	1014.80 1031.24 1063.34	3173 3175	
1277.79 1286.42 1314.16	1131.33 1311.38 1339 61		
1351.20 1359.77 1386.62	1354.05 1356.95 1371.65		
1389.60 1397.88 1402.98	1389.81 1394.12 1397.56		
1403.73 1404.08 1407.60	1401.17 1411.34 1429.60		
1411.79 1416.78 1432.75	1580.09 1849.90 3053.94		
3031.90 3068.05 3073.63	3076.06 3078.28 3080.10		
3078.69 3078.96 3081.08	3082.51 3083.73 3124.29		
3088.68 3089.85 3145.91	3134.41 3138.72 3174.58		
3180.09 3181.10 3184.05	3175.50		

TS IIB. 3 Information for C2C=C Related Transition States

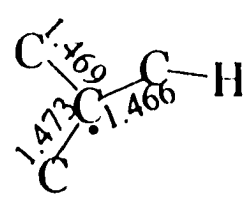
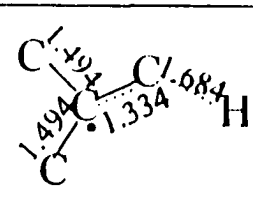
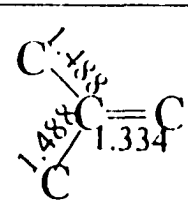
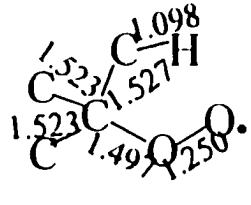
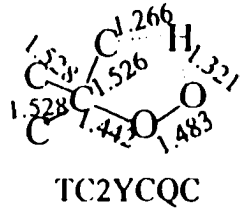
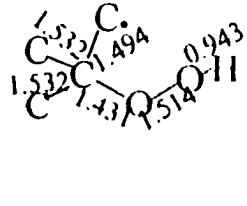
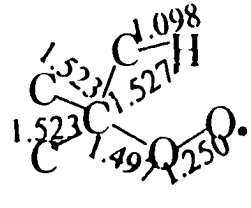
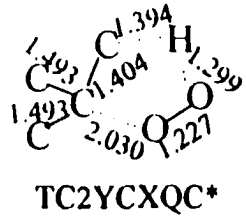
Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
TS 1	Rx C3C. = TC2CJ*CXH S {cal/mol K} 75.100 74.350 for A(T) = Aprime * T^n Aprime = 6.1488E+09 n = 1.33029 Rx C3C. = C2C*C + H Hf {Kcal/mol} 11.900 -3.800 52.100 S {cal/mol K} 75.100 71.010 27.300 dU (dE) {kcal/mol} (") = 35.81 dUr avg (298., 1500. K) = 35.82 Fit Af/Ar: A = 3.065E-02 n = .75 alpha = 8.028E-04		 TC2J*CXH	
TS 2	Rx C3CQ. = TC2YCQC S {cal/mol K} 83.360 82.050 for A(T) = Aprime * T^n Aprime = 7.5198E+09 n = 1.22128 Rx C3CQ. = C3.CQ Hf {Kcal/mol} -23.580 -10.680 S {cal/mol K} 83.360 92.190 dU (dE) {kcal/mol} (") = 12.90 dUr avg (298., 1500. K) = 13.50 Fit Af/Ar: A = 6.146E-02 n = 1.31 alpha = 8.741E-04		 TC2YCQC	
TS 3	Rx C3CQ. = TC2YCXQC* S {cal/mol K} 83.360 84.540 for A(T) = Aprime * T^n Aprime = 2.8762E+10 n = 1.21961 Rx C3CQ. = C2C*C + HO_2 Hf {Kcal/mol} -23.580 -3.800 3.500 S {cal/mol K} 83.360 71.010 54.730 dHr {kcal/mol} (298K) = 23.28		 TC2YCXQC*	

Table IIB. 3 Information for C2C=C Related Transition States (Cont')

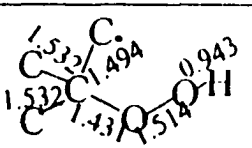
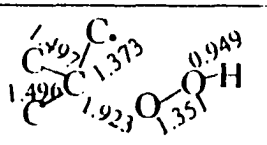
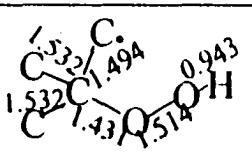
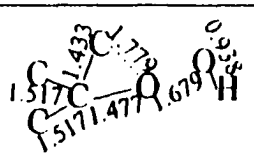
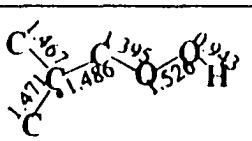
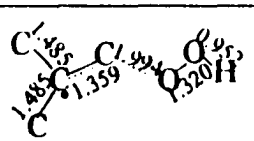
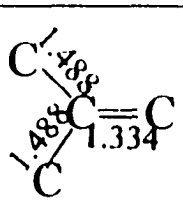
Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
	dHr avg (298., 1500. K) = 21.17 dU (dE) {kcal/mol} (") = 22.69 dUr avg (298., 1500. K) = 19.38 Fit Af/Ar: A = 8.789E+10 n = -2.59 alpha = 1.937E-04			
TS 4	Rx C3.CQ = TC3*CXQ S {cal/mol K} 92.190 90.910 for A(T) = Aprime * T^n Aprime = 1.0628E+13 n = -.02701 Rx C3.CQ = C2C*C + HO_2 Hf {Kcal/mol} -10.680 -3.800 3.500 S {cal/mol K} 92.190 71.010 54.730 dHr {kcal/mol} (298K) = 10.38 dHr avg (298., 1500. K) = 7.67 dU (dE) {kcal/mol} (") = 9.79 dUr avg (298., 1500. K) = 5.88 Fit Af/Ar: A = 1.430E+12 n = -3.90 alpha =-6.804E-04		 TC3*CXQ	
TS 5	Rx C3.CQ = TC2YC2OXP S {cal/mol K} 92.190 86.990 for A(T) = Aprime * T^n Aprime = 1.3840E+12 n = -.03057		 TC2YC2OXP	
TS 6	Rx C2C*C + HO_2 = TC2CJ*CXQ S {cal/mol K} 71.010 54.730 91.280 for A(T) = Aprime * T^n Aprime = 6.3904E+02 n = 3.10237 Rx C2C*C + HO_2 = C2C.CQ		 TC2CJ*CXQ	

Table IIB. 3 Information for C2C=C Related Transition States (Cont')

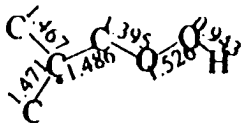
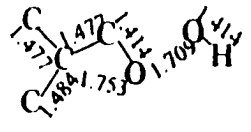
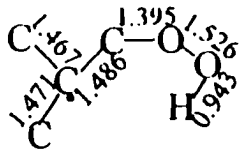
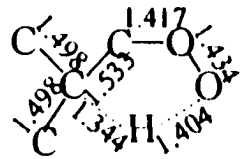
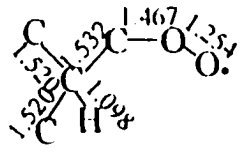
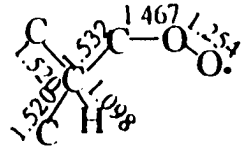
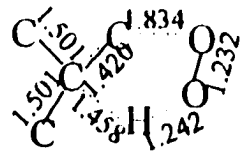
Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
	Hf {Kcal/mol} -3.800 3.500 -9.290 S {cal/mol K} 71.010 54.730 97.760 dHr {kcal/mol} (298K) = -8.99 dHr avg (298., 1500. K) = -7.58 dU (dE) {kcal/mol} (") = -8.40 dUr avg (298., 1500. K) = -5.79 Fit Af/Ar: A = 4.161E-07 n = 2.03 alpha =-1.597E-04			
TS 7	Rx C2C.CQ = TC2YCCOXP S {cal/mol K} 97.760 87.970 for A(T) = Aprime * T^n Aprime = 2.9956E+08 n = 1.06135		 TC2YCCOXP	
TS 8	Rx C2C.CQ = TC2YCCQ S {cal/mol K} 97.760 83.170 for A(T) = Aprime * T^n Aprime = 3.3144E+05 n = 1.79209 Rx C2C.CQ = C2CCQ. Hf {Kcal/mol} -9.290 -17.590 S {cal/mol K} 97.760 89.440 dU (dE) {kcal/mol} (") = -8.30 dUr avg (298., 1500. K) = -7.89 Fit Af/Ar: A = 7.503E-03 n = .10 alpha =-2.761E-04		 TC2YCCQ	
TS 9	Rx C2CCQ. = TC2YC*CXQ S {cal/mol K} 89.440 82.610 for A(T) = Aprime * T^n Aprime = 7.4672E+09 n = .73486 Rx C2CCQ. = C2C*C + HO_2 Hf {Kcal/mol} -17.590 -3.800 3.500 S {cal/mol K} 89.440 71.010 54.730		 TC2YC*CXQ	

Table IIB. 3 Information for C2C=C Related Transition States (Cont')

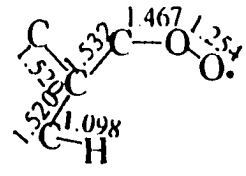
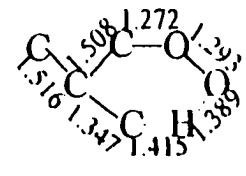
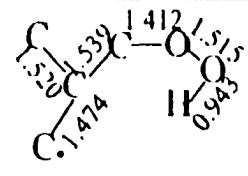
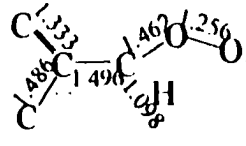
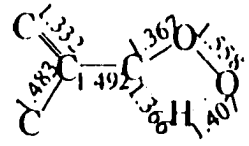
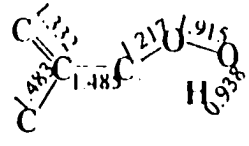
Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
	dHr (kcal/mol) (298K) = 17.29 dHr avg (298., 1500. K) = 15.46 dU (dE) (kcal/mol) (") = 16.70 dUr avg (298., 1500. K) = 13.68 Fit Af/Ar: A = 3.203E+08 n = -2.13 alpha = 4.358E-04			
TS 10	Rx C2CCQ. = TCYCCQC S (cal/mol K) 89.440 80.340 for A(T) = Aprime * T^n Aprime = 7.2022E+07 n = 1.31680 Rx C2CCQ. = C2.CCQ Hf (Kcal/mol) -17.590 -4.690 S (cal/mol K) 89.440 96.380 dU (dE) (kcal/mol) (") = 12.90 dUr avg (298., 1500. K) = 13.69 Fit Af/Ar: A = 3.707E-03 n = 1.65 alpha = 1.074E-03		 TCYCCQC	
TS 11	Rx C*CICCQ. = TC2*CYCQ S (cal/mol K) 89.740 86.820 for A(T) = Aprime * T^n Aprime = 1.0112E+09 n = 1.45505 Rx C*CICCQ. = C*CICC.Q Hf (Kcal/mol) 11.720 9.120 S (cal/mol K) 89.740 90.110 dU (dE) (kcal/mol) (") = -2.60 dUr avg (298., 1500. K) = -1.03 Fit Af/Ar: A = 3.062E-06 n = 2.31 alpha = 1.095E-03	 C=C(C)COO.	 TC2*CYCQ	 C=C(C)C.OOH

Table IIB. 3 Information for C2C=C Related Transition States (Cont')

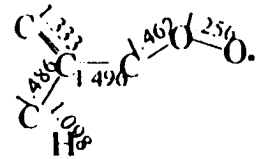
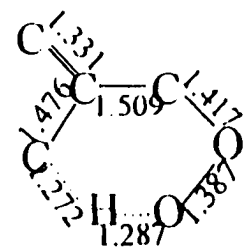
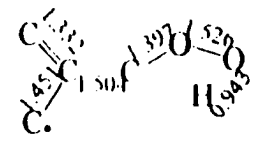
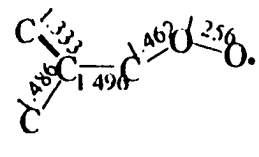
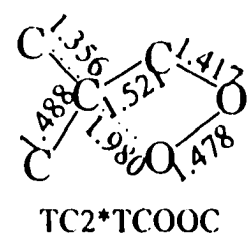
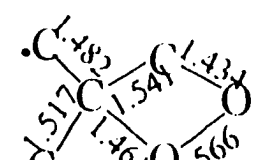
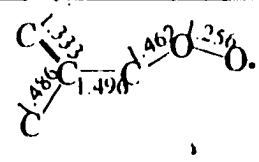
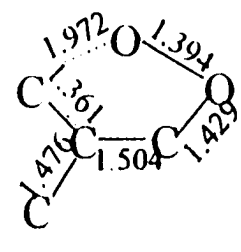
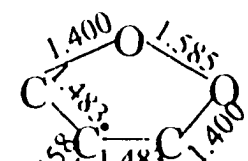
Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
TS 12	Rx C*CICCQ. = TC*YCCQC S {cal/mol K} 89.740 79.760 for A(T) = Aprime * T^n Aprime = 1.2748E+06 n = 1.95375 Rx C*CICCQ. = C*CIC.CQ Hf {Kcal/mol} 11.720 11.720 S {cal/mol K} 89.740 91.200 dU (dE) {kcal/mol} (") = .00 dUr avg (298., 1500. K) = 1.54 Fit Af/Ar: A = 1.037E-05 n = 2.18 alpha = 9.729E-04		 TC*YCCQC	
TS 13	Rx C*CICCQ. = TC2*YCOOC S {cal/mol K} 89.740 82.170 for A(T) = Aprime * T^n Aprime = 1.2216E+09 n = .98999 Rx C*CICCQ. = C2.CYCOOC Hf {Kcal/mol} 11.720 27.810 S {cal/mol K} 89.740 83.740 dU (dE) {kcal/mol} (") = 16.09 dUr avg (298., 1500. K) = 17.02 Fit Af/Ar: A = 2.393E-03 n = .49 alpha =-3.097E-04		 TC2*TCOOC	
TS 14	Rx C*CICCQ. = TCYC*COOC S {cal/mol K} 89.740 79.360 for A(T) = Aprime * T^n Aprime = 4.0903E+08 n = .92337 Rx C*CICCQ. = CCYC.COOC Hf {Kcal/mol} 11.720 9.840 S {cal/mol K} 89.740 81.750 dU (dE) {kcal/mol} (") = -1.88 dUr avg (298., 1500. K) = -.86 Fit Af/Ar: A = 5.813E-03 n = .14 alpha =-7.725E-04		 TCYC*COOC	

Table IIB. 3 Information for C2C=C Related Transition States (Cont')

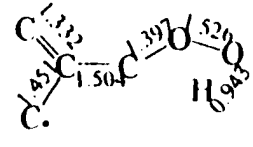
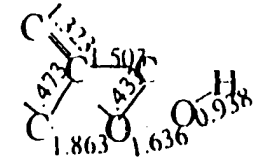
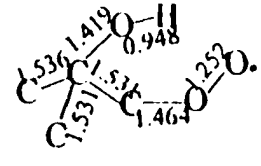
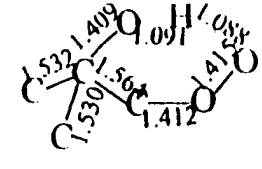
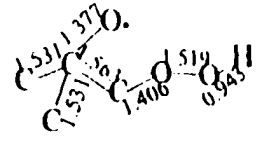
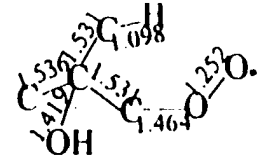
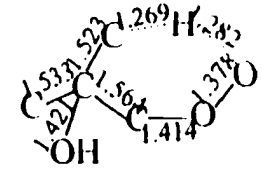
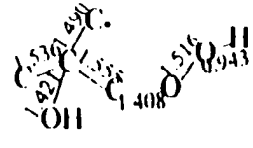
Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
TS 15	Rx C*ClC.CQ = TC*YC3OXP S {cal/mol K} 91.200 84.330 for A(T) = Aprime * T^n Aprime = 1.2156E+12 n = -.17298		 TC*YC3OXP	
TS 16	Rx C2COHCQ. = TC2YCCQO S {cal/mol K} 96.020 84.300 for A(T) = Aprime * T^n Aprime = 7.5594E+07 n = 1.06165 Rx C2COHCQ. = C2CO.CQ Hf {Kcal/mol} -60.190 -44.330 S {cal/mol K} 96.020 96.600 dU (dE) {kcal/mol} (") = 15.86 dUr avg (298., 1500. K) = 15.38 Fit Af/Ar: A = 3.536E-02 n = .70 alpha = 1.134E-03		 TC2YCCQO	
TS 17	Rx C2COHCQ. = TICPYCCQC S {cal/mol K} 96.020 85.370 Aprime = 1.2631E+08 n = 1.08388 Rx C2COHCQ. = C2.COHCQ Hf {Kcal/mol} -60.190 -47.290 S {cal/mol K} 96.020 100.360 dU (dE) {kcal/mol} (") = 12.90 dUr avg (298., 1500. K) = 13.09 Fit Af/Ar : A = 2.829E-02 n = 1.07 alpha = 9.692E-04		 TICPYCCQC	

Table IIB. 3 Information for C2C=C Related Transition States (Cont')

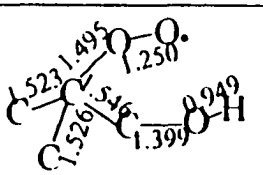
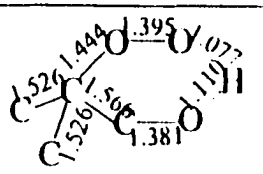
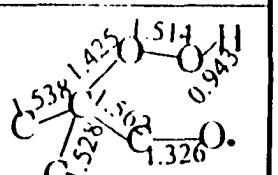
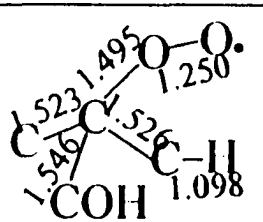
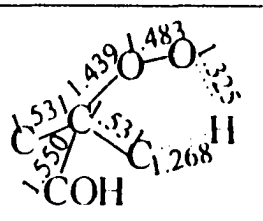
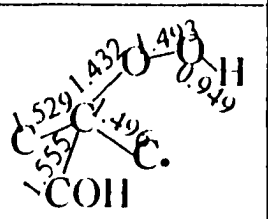
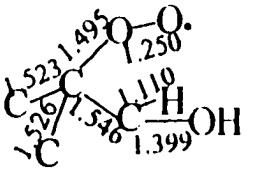
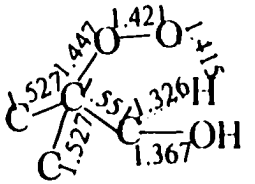
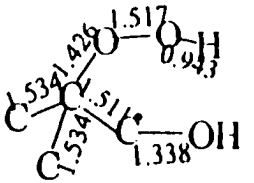
Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
TS 18	Rx C2CQ.COH = TC2YCQOC S {cal/mol K} 96.140 84.710 for A(T) = Aprime * T^n Aprime = 4.2170E+07 n = 1.18430 Rx C2CQ.COH = C2CQCO. Hf {Kcal/mol} -59.380 -43.520 S {cal/mol K} 96.140 95.170 dU (dE) {kcal/mol} (") = 15.86 dUr avg (298., 1500. K) = 17.30 Fit Af/Ar: A = 2.475E-04 n = 1.36 alpha = 1.870E-04		 TC2YCQOC	
TS 19	Rx C2CQ.COH = TICCPYCQC S {cal/mol K} 96.140 91.890 for A(T) = Aprime * T^n Aprime = 3.8358E+09 n = 1.07094 Rx C2CQ.COH = C2.CQCOH Hf {Kcal/mol} -59.380 -46.480 S {cal/mol K} 96.140 103.990 dU (dE) {kcal/mol} (") = 12.90 dUr avg (298., 1500. K) = 13.59 Fit Af/Ar: A = 2.231E-02 n = 1.40 alpha = 8.977E-04		 TICCPYCQC	
TS 20	Rx C2CQ.COH = TC2YCQCIP S {cal/mol K} 96.140 89.510 for A(T) = Aprime * T^n Aprime = 2.3281E+08 n = 1.35787 Rx C2CQ.COH = C2CQC.OH Hf {Kcal/mol} -59.380 -53.580 S {cal/mol K} 96.140 100.100 dU (dE) {kcal/mol} (") = 5.80		 TC2YCQCIP	

Table IIB. 3 Information for C2C=C Related Transition States (Cont')

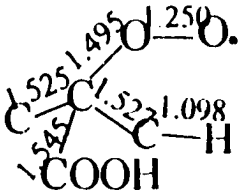
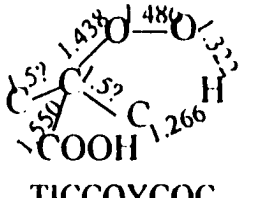
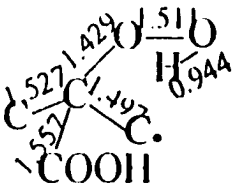
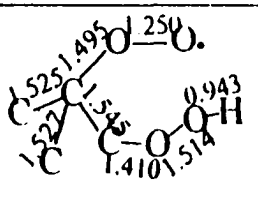
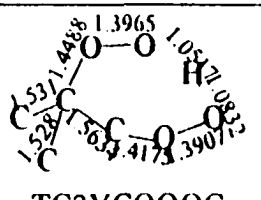
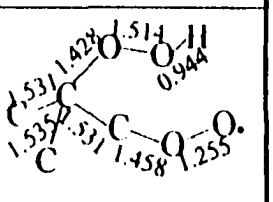
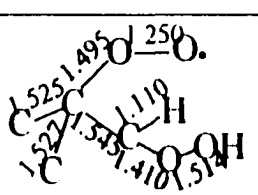
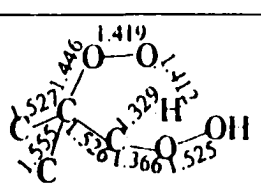
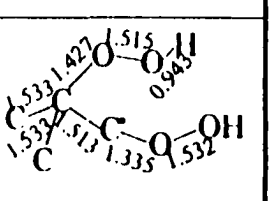
Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
	dUr avg (298., 1500. K) = 6.46 Fit Af/Ar: A = 3.233E-03 n = 1.41 alpha = 9.274E-04			
TS 21	Rx C2CQ.CQ = TICCQYCQC S {cal/mol K} 102.620 101.000 for A(T) = Aprime * T^n Aprime = 1.8018E+08 n = 1.83229 Rx C2CQ.CQ = C2.CQCQ Hf {Kcal/mol} -47.670 -31.870 S {cal/mol K} 102.620 110.040 dU (dE) {kcal/mol} (") = 15.80 dUr avg (298., 1500. K) = 16.33 Fit Af/Ar: A = 3.369E-02 n = 1.30 alpha = 9.308E-04		 TICCQYCQC	
TS 22	Rx C2CQ.CQ = TC2YCQOOC S {cal/mol K} 102.620 86.090 for A(T) = Aprime * T^n Aprime = 3.5366E+12 n = -1.24370 Rx C2CQ.CQ = C2CQCQ. Hf {Kcal/mol} -47.670 -44.770 S {cal/mol K} 102.620 102.680 dU (dE) {kcal/mol} (") = 2.90 dUr avg (298., 1500. K) = 3.11 Fit Af/Ar: A = 8.358E-01 n = .02 alpha = -1.595E-04		 TC2YCQOOC	
TS 23	Rx C2CQ.CQ = TC2YCQCIQ S {cal/mol K} 102.620 98.220 for A(T) = Aprime * T^n Aprime = 1.3902E+07 n = 2.03199 Rx C2CQ.CQ = C2CQC.Q Hf {Kcal/mol} -47.670 -36.970		 TC2YCQCIQ	

Table IIB. 3 Information for C2C=C Related Transition States (Cont')

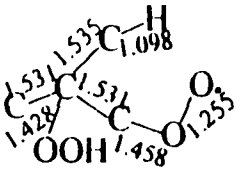
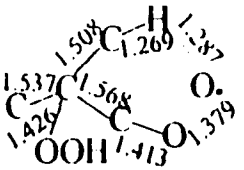
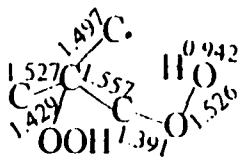
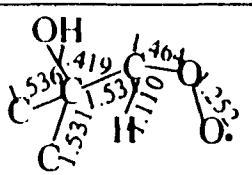
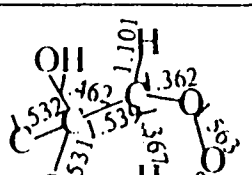
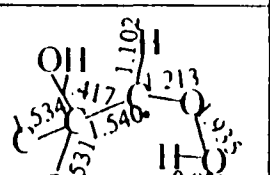
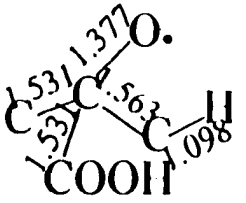
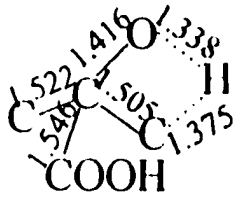
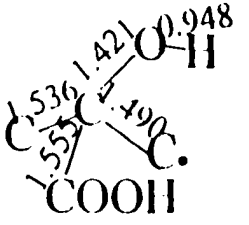
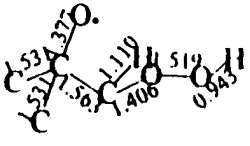
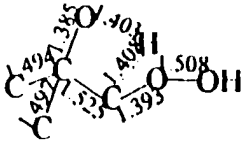
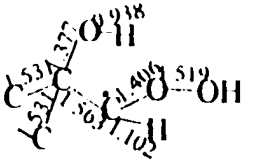
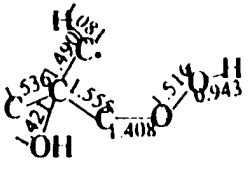
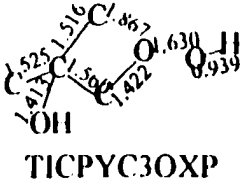
Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
	S {cal/mol K} 102.620 106.930 dU (dE) {kcal/mol} (") = 10.70 dUr avg (298., 1500. K) = 11.43 Fit Af/Ar: A = 6.883E-03 n = 1.29 alpha = 7.553E-04			
TS 24	Rx C2CQCQ. = TICQYCCQC S {cal/mol K} 102.680 95.340 for A(T) = Aprime * T^n Aprime = 6.1059E+07 n = 1.49680 Rx C2CQCQ.= C2.CQCQ Hf {Kcal/mol} -44.770 -31.870 S {cal/mol K} 102.680 110.040 dU (dE) {kcal/mol} (") = 12.90 dUr avg (298., 1500. K) = 13.22 Fit Af/Ar : A = 4.031E-02 n = 1.28 alpha = 1.090E-03		 TICQYCCQC	
TS 25	Rx C2COHCQ. = TC2CPYCQ S {cal/mol K} 96.020 92.020 for A(T) = Aprime * T^n Aprime = 3.1162E+09 n = 1.17380 Rx C2COHCQ. = C2COHC.Q Hf {Kcal/mol} -60.190 -52.390 S {cal/mol K} 96.020 103.010 dU (dE) {kcal/mol} (") = 7.80 dUr avg (298., 1500. K) = 8.21 Fit Af/Ar: A = 1.172E-02 n = 1.47 alpha = 1.211E-03		 TC2CPYCQ	

Table IIB. 3 Information for C2C=C Related Transition States (Cont')

Number	Thermodynamic Properties Information	Reactant	Transition State*	Product
TS 26	Rx C2CO.CQ = TICCQYCPC S {cal/mol K} 96.600 92.500 for A(T) = Aprime * T^n Aprime = 7.3487E+05 n = 2.54484 Rx C2CO.CQ = C2.COHCQ Hf {Kcal/mol} -44.330 -47.290 S {cal/mol K} 96.600 100.360 dU (dE) {kcal/mol} (") = -2.96 dUr avg (298., 1500. K) = -2.29 Fit Af/Ar: A = 8.001E-01 n = .36 alpha = -1.651E-04		 TICCQYCPC	
TS 27	Rx C2CO.CQ = TC2YCPCIQ S {cal/mol K} 96.600 88.690 for A(T) = Aprime * T^n Aprime = 2.5418E+06 n = 1.99355 Rx C2CO.CQ = C2COHC.Q Hf {Kcal/mol} -44.330 -52.390 S {cal/mol K} 96.600 103.010 dU (dE) {kcal/mol} (") = -8.06 dUr avg (298., 1500. K) = -7.17 Fit Af/Ar: A = 3.315E-01 n = .77 alpha = 7.659E-05		 TC2YCPCIQ	
TS 28	Rx C2.COHCQ = TICPYC3OXP S {cal/mol K} 100.360 90.950 for A(T) = Aprime * T^n Aprime = 4.2531E+10 n = .18330		 TICPYC3OXP	

* T = Transition state; Y = Cyclic, Q = OOH; Q. = OO., P = OH; I = iso-C; X = represents the elimination of the species after X (except for TC2YCXQC*)

TS IIB. 4 Transition State Information for Reaction $CH_3OH \rightarrow CH_2O + H_2$

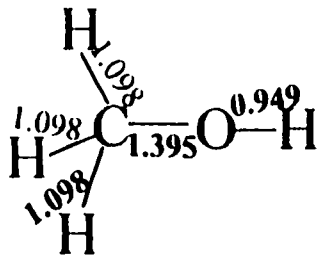
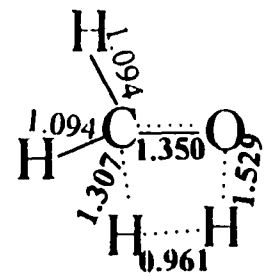
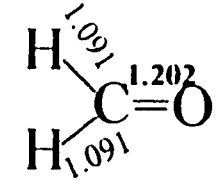
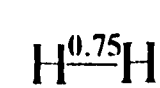
Reactant	Transition State	Product 1	Product 2
			
CH_3OH	TSMEOH	CH_2O	H_2
Principle moments of inertia in unit of cm^{-1}: A = 4.244786 B = 0.856787 C = 0.825179 in unit of 10^{-40}-gram-cm^2: A = 6.594594 B = 32.671649 C = 33.923121	Principle moments of inertia in unit of cm^{-1}: A = 3.173265 B = 0.929231 C = 0.837343 in unit of 10^{-40}-gram-cm^2: A = 8.821400 B = 30.124509 C = 33.430301	Principle moments of inertia in unit of cm^{-1}: A = 9.720866 B = 1.305991 C = 1.151313 in unit of 10^{-40}-gram-cm^2: A = 2.879645 B = 21.434012 C = 24.313656	* Thermodynamic data from THERM - Group Additivity
Symmetry = 3	Symmetry = 1	Symmetry = 1	
Internal rotor(s): V / kcal-mol^{-1} CH_3-OH (1): 1.09	No Internal Rotor	No Internal Rotor	
frequencies 292.33 988.92 1020.76 1164.45 1362.29 1366.05 1366.27	frequencies -3495.48 598.78 916.88 1002.25 1127.97 1145.21	frequencies 1070 1098 1289 1987 2999 3026	

Table IIB. 4 Transition State Information for $CH_3OH \rightarrow CH_2O + H_2$ (Cont')

1409.05 3035.71 3068.61 3141.15 3896.48	1315.87 1487.04 1844.70 2486.70 3003.12 3012.59		

TS IIB. 5 Thermodynamic Analysis for C3COC → C2C=C + CH_3OH

	Rx	C3COC	= TMTBE
	Hf {Kcal/mol}	-68.900	-1.300
	S {cal/mol K}	85.640	86.370
	dU (dE) {kcal/mol} (298K) =		67.60
	dUr avg (298., 1500. K) =		67.86
	for A(T) = Aprime * T^n		
	Aprime = 2.20E+10		n = 1.22396

Rx	C3COC = C2C*C + CH3OH				
Hf {Kcal/mol}	-68.9	-3.8	-48		
S {cal/mol K}	85.85	69.99	57.3		
dHr {kcal/mol} (298K) = 17.1 dHr avg (298., 1500. K) = 15.19					
dU (dE) {kcal/mol} (") = 16.51 dUr avg (298., 1500. K) = 13.4					
Af/Ar (") = 1.717E+04 Af/Ar avg (298., 1500. K) = 1.750E+03					
Fit Af/Ar: A = 6.14E+09 n = -2.19 alpha = 4.42E-04					

Temp(K)	AF(T)	AF-fit(T)	dS(cal/mol K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300	2.45E+13	2.36E+13	8.11E-50	1.71E+01	1.65E+01	4.14E+01	1.70E+04	4.67E+00
400	3.34E+13	3.36E+13	1.67E-37	1.70E+01	1.62E+01	4.11E+01	1.08E+04	5.38E-01
500	4.34E+13	4.42E+13	4.11E-30	1.67E+01	1.57E+01	4.06E+01	6.61E+03	-3.55E+00
600	5.42E+13	5.52E+13	3.50E-25	1.64E+01	1.52E+01	4.00E+01	4.11E+03	-7.58E+00
800	7.78E+13	7.85E+13	5.16E-19	1.57E+01	1.41E+01	3.89E+01	1.82E+03	-1.55E+01
1000	1.03E+14	1.03E+14	2.63E-15	1.50E+01	1.30E+01	3.81E+01	9.62E+02	-2.32E+01
1200	1.29E+14	1.29E+14	7.84E-13	1.43E+01	1.19E+01	3.75E+01	5.84E+02	-3.07E+01
1500	1.69E+14	1.70E+14	2.36E-10	1.33E+01	1.03E+01	3.68E+01	3.23E+02	-4.19E+01
2000	2.47E+14	2.41E+14	7.23E-08	1.18E+01	7.79E+00	3.59E+01	1.56E+02	-6.00E+01

TS IIB. 6 Thermodynamic Analysis for $CH_3OH \rightarrow CH_2O + H_2$

	Rx CH_3OH = TMEOH			Rx $CH_3OH = CH_2O + H_2$				
	Hf {Kcal/mol} -48.000 45.060			Hf {Kcal/mol} -48.00 -26.00 0				
	S {cal/mol K} 57.260 54.870			S {cal/mol K} 57.30 50.92 31.20				
	dU (dE) {kcal/mol} (298K) = 93.06			dHr {kcal/mol} (298K) = 22.0 dHr avg (298., 1500 K) = 22.89				
	dUr avg (298., 1500. K) = 93.41			dU (dE) {kcal/mol} (") = 21.41 dUr avg (298., 1500 K) = 21.11				
	for A(T) = Aprime * T^n			Af/Ar (") = 4.000E+00 Af/Ar avg (298., 1500 K) = 3.244E+00				
	Aprime = 3.02E+09 n = 1.29165			Fit Af/Ar: A = 1.23E-03 n = 1.54 alpha = 1.94E-03				
Temp(K)	AF(T)	AF-fit(T)	dS(cal/mol K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300	5.10E+12	4.78E+12	4.76E-69	2.20E+01	2.14E+01	2.49E+01	4.04E+00	1.46E+01
400	6.75E+12	6.93E+12	4.23E-52	2.25E+01	2.17E+01	2.61E+01	5.76E+00	1.20E+01
500	8.83E+12	9.24E+12	6.28E-42	2.28E+01	2.18E+01	2.69E+01	6.93E+00	9.34E+00
600	1.13E+13	1.17E+13	3.83E-35	2.31E+01	2.19E+01	2.75E+01	7.55E+00	6.62E+00
800	1.69E+13	1.70E+13	1.19E-26	2.35E+01	2.19E+01	2.81E+01	7.64E+00	1.06E+00
1000	2.30E+13	2.26E+13	1.50E-21	2.37E+01	2.18E+01	2.83E+01	6.95E+00	-4.58E+00
1200	2.93E+13	2.86E+13	3.84E-18	2.38E+01	2.14E+01	2.84E+01	6.04E+00	-1.03E+01
1500	3.89E+13	3.82E+13	9.94E-15	2.38E+01	2.08E+01	2.84E+01	4.76E+00	-1.88E+01
2000	5.48E+13	5.54E+13	2.61E-11	2.34E+01	1.94E+01	2.82E+01	3.19E+00	-3.29E+01

APPENDIX IIC

FIGURES IN THE MTBE SYSTEM

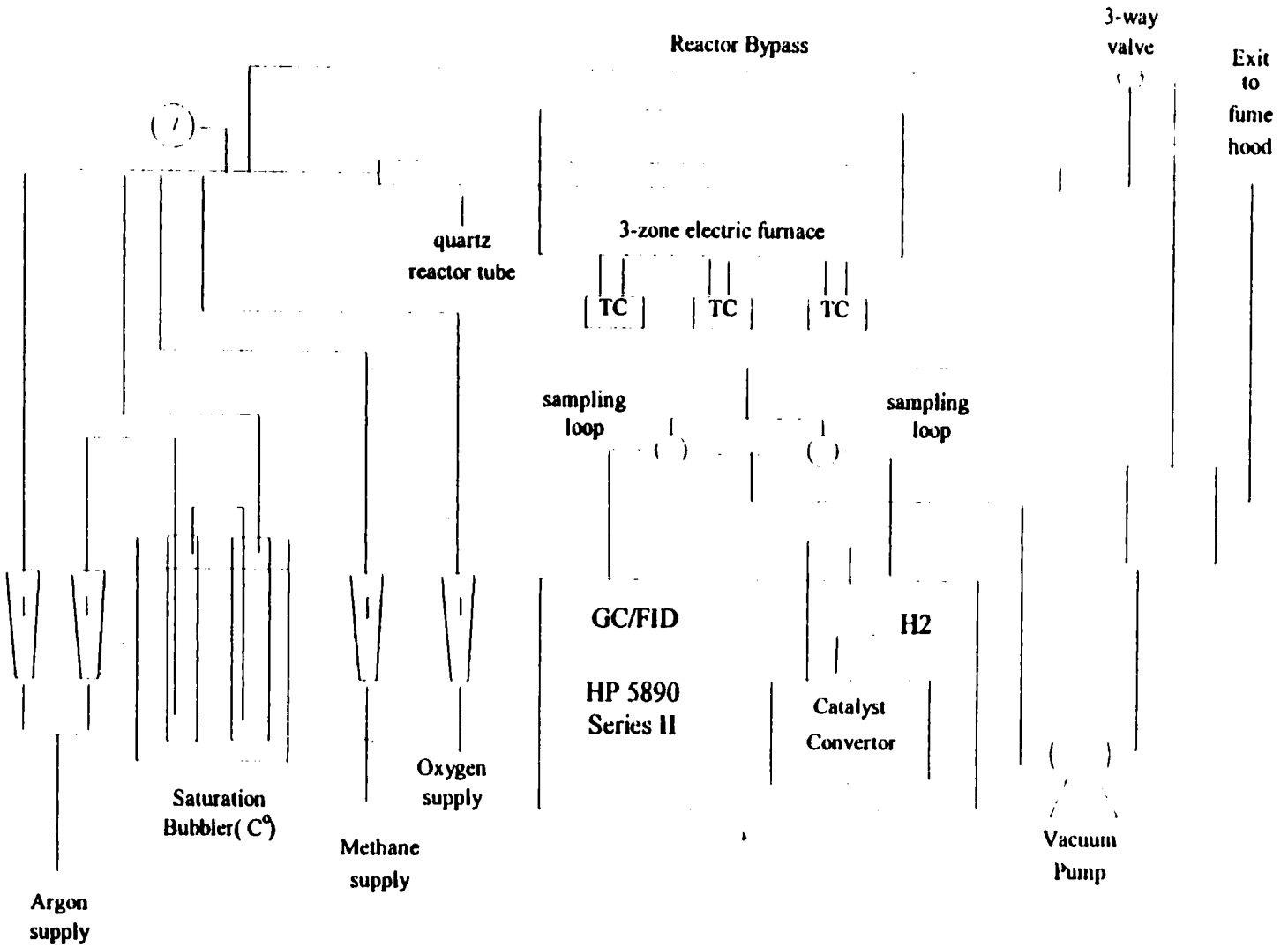


Figure IIC. 1 Experimental Apparatus

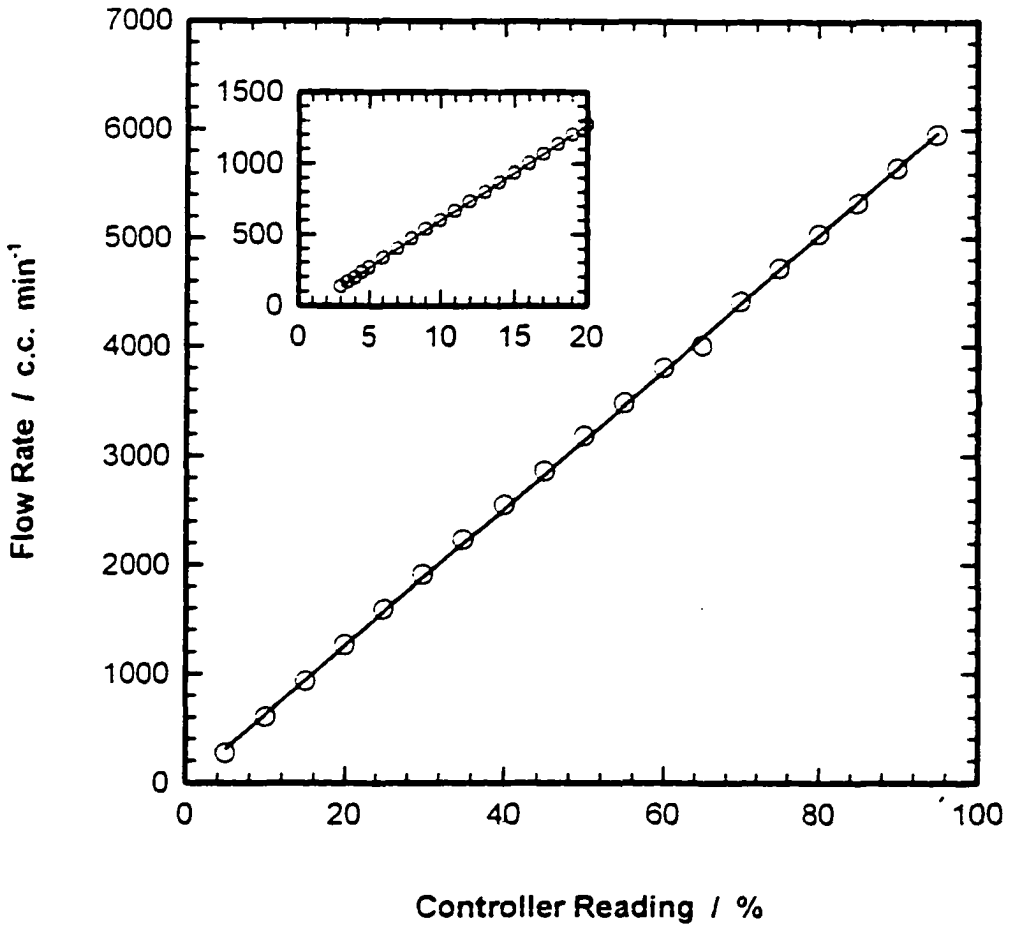


Figure IIC. 2 Calibration curve of mass flow controller 1 (AR) with inlet pressure of 200 psi.

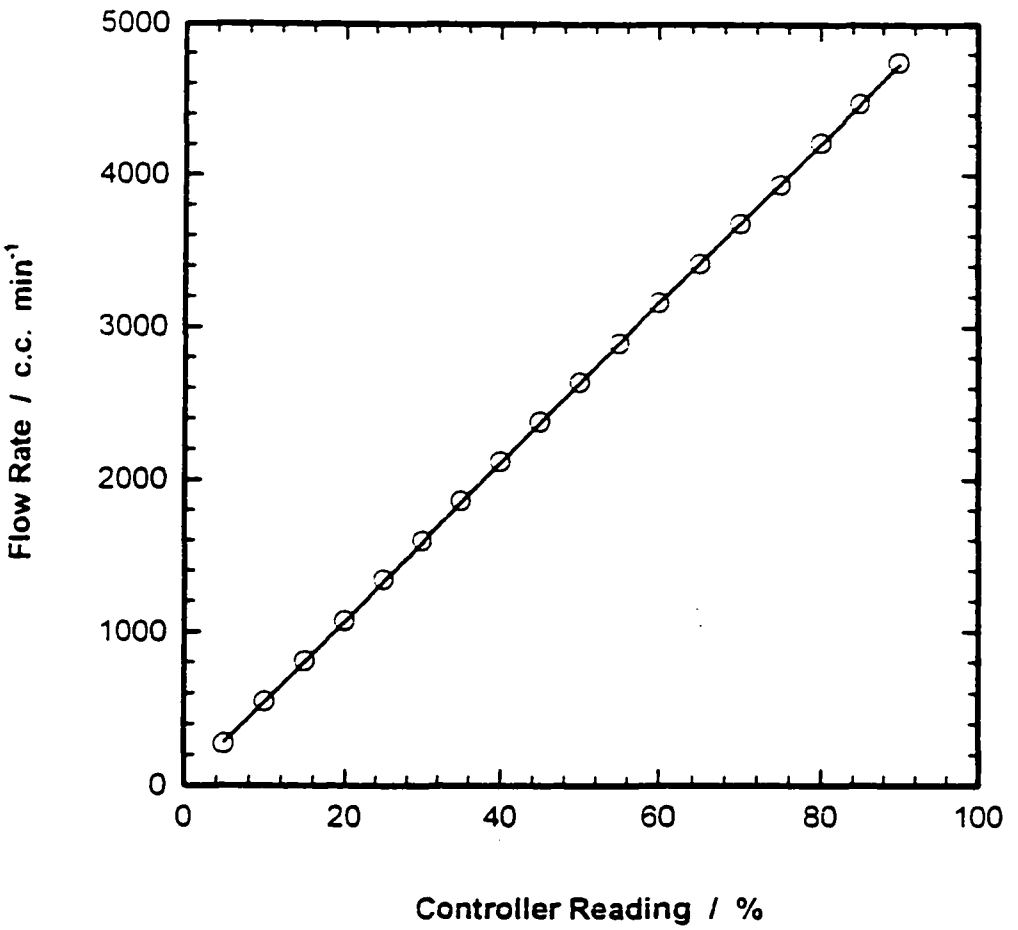


Figure IIC. 3 Calibration curve of mass flow controller 2 (AR) with inlet pressure of 200 psi.

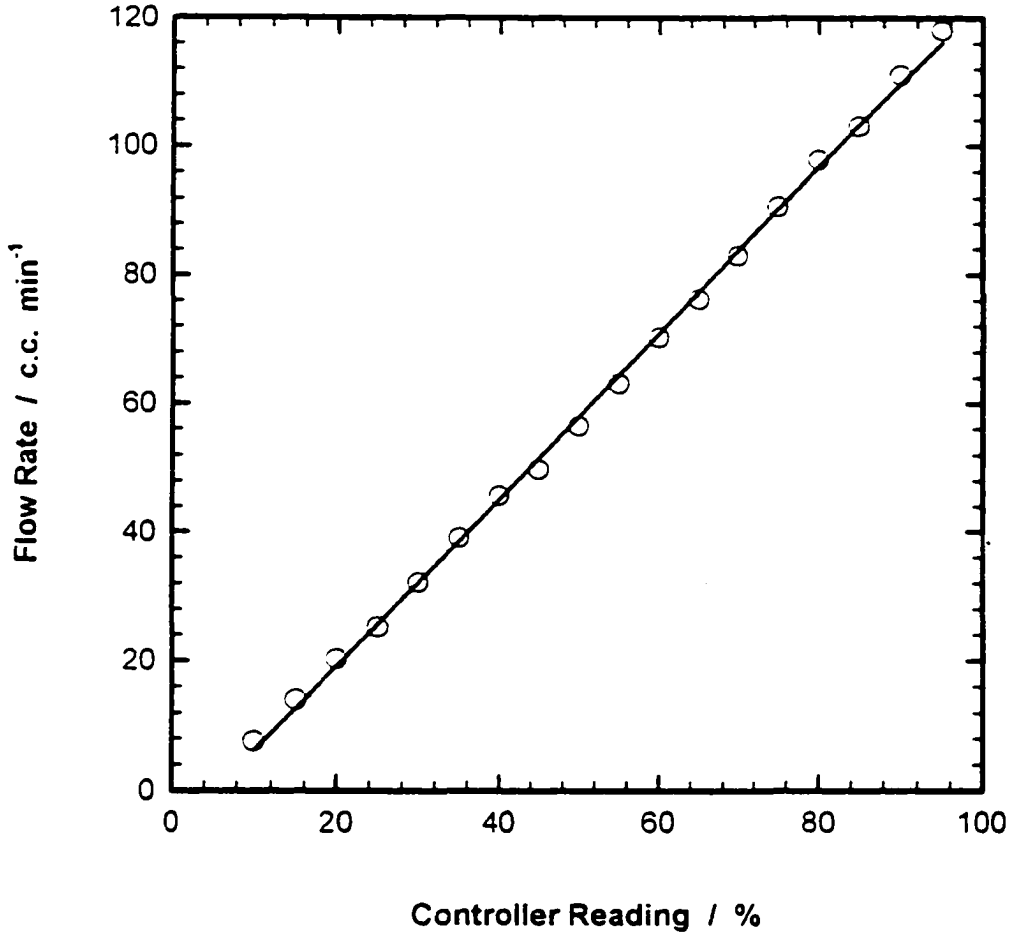


Figure IIC. 4 Calibration curve of mass flow controller 3 (O_2) with inlet pressure of 200 psi.

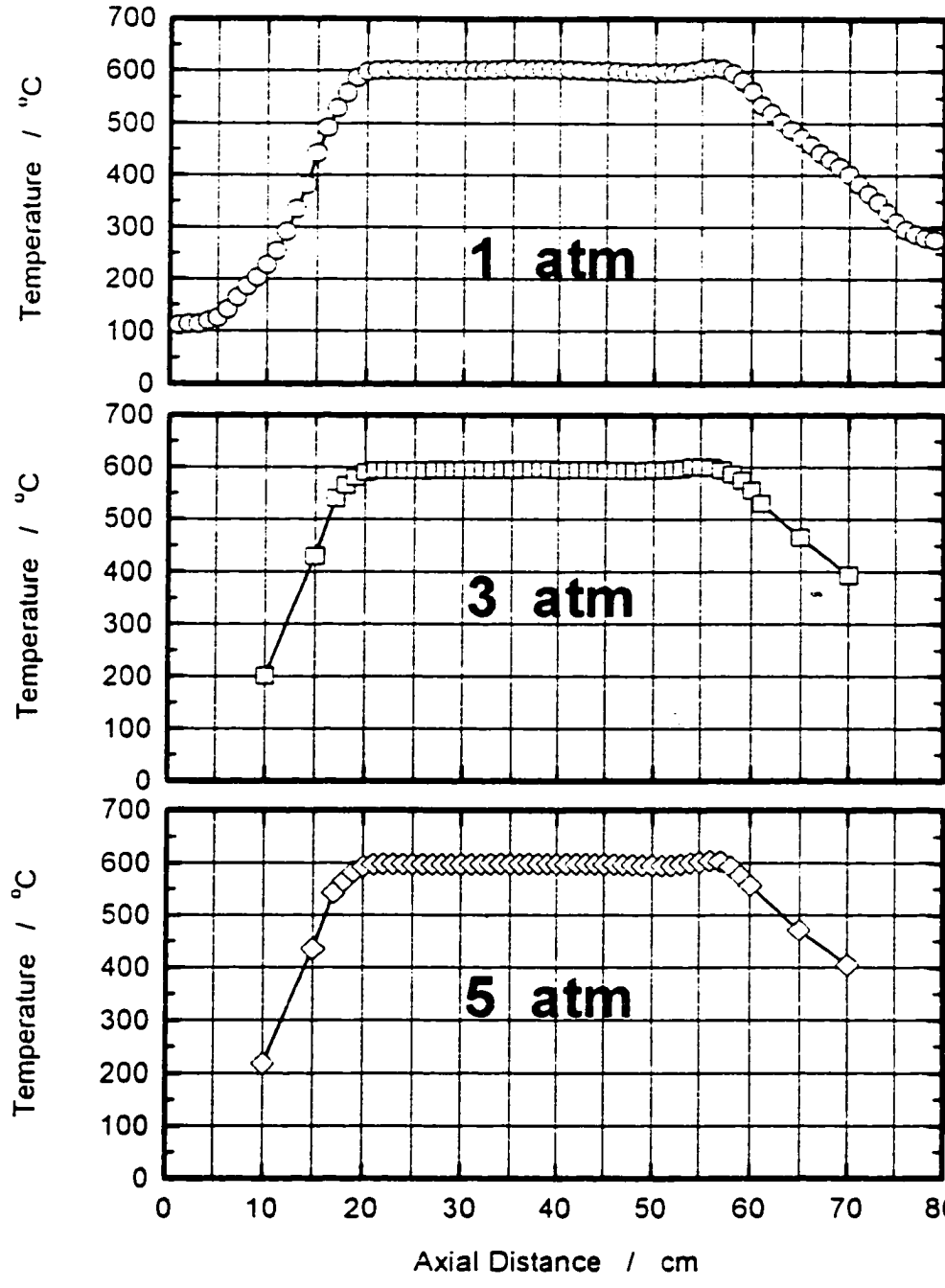


Figure IIC. 5 Reactor temparature profile at 1.3 gm Ar / min.

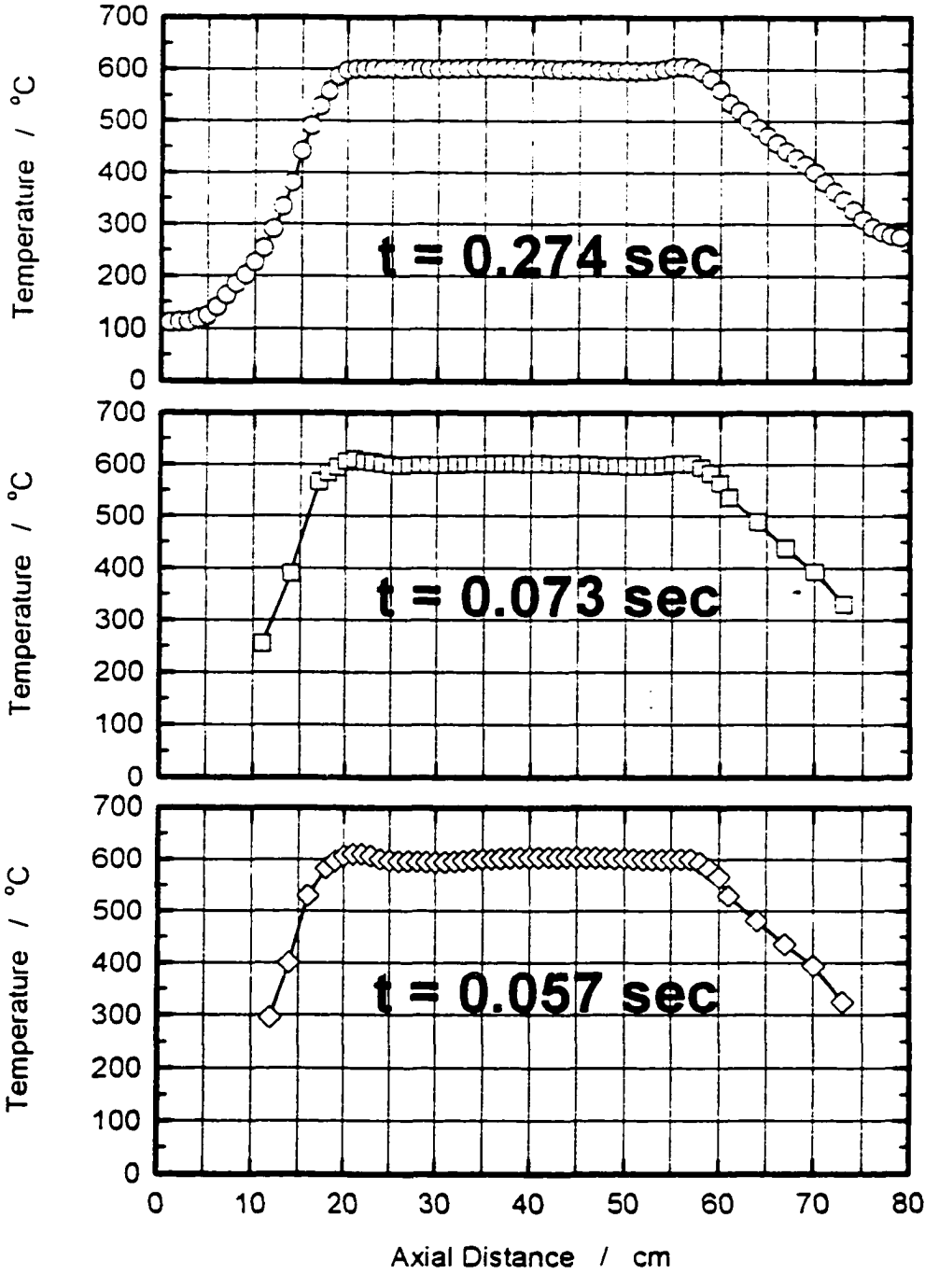


Figure IIC. 6 Reactor temperature profiles at 1 atm.

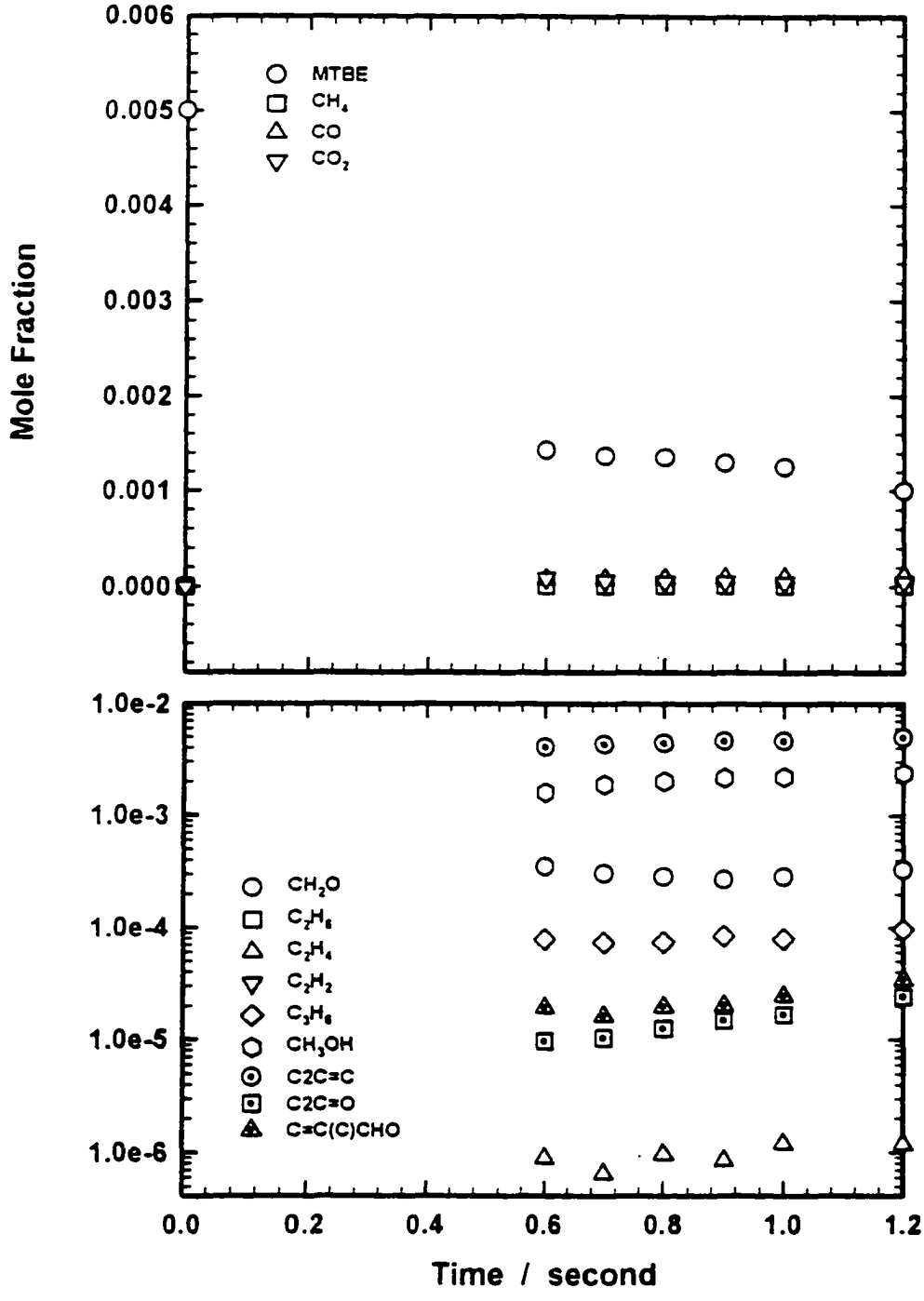


Figure IIC. 7 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 4 atm, T = 823 K

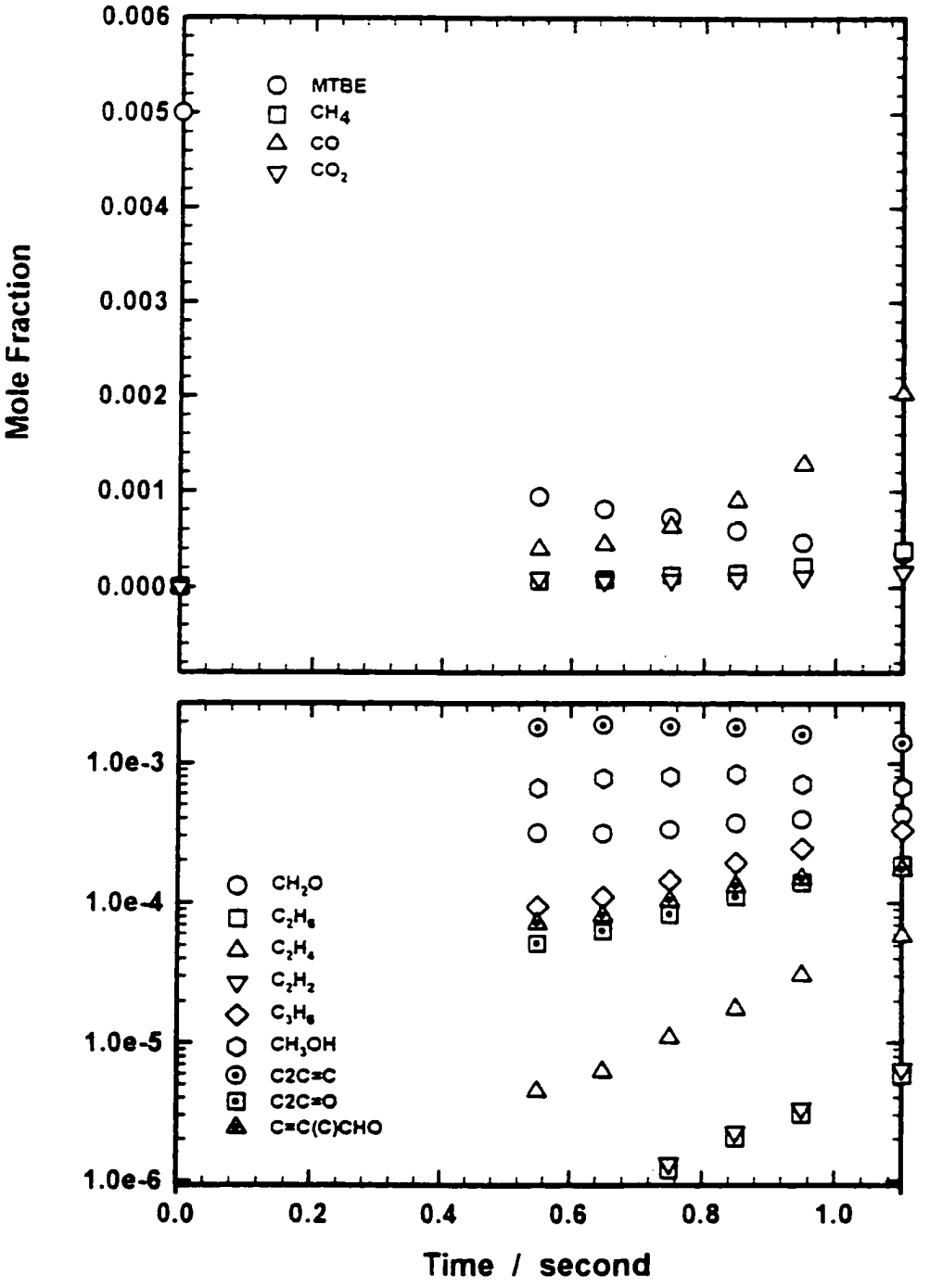


Figure IIC. 8 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 4 atm, T = 873 K

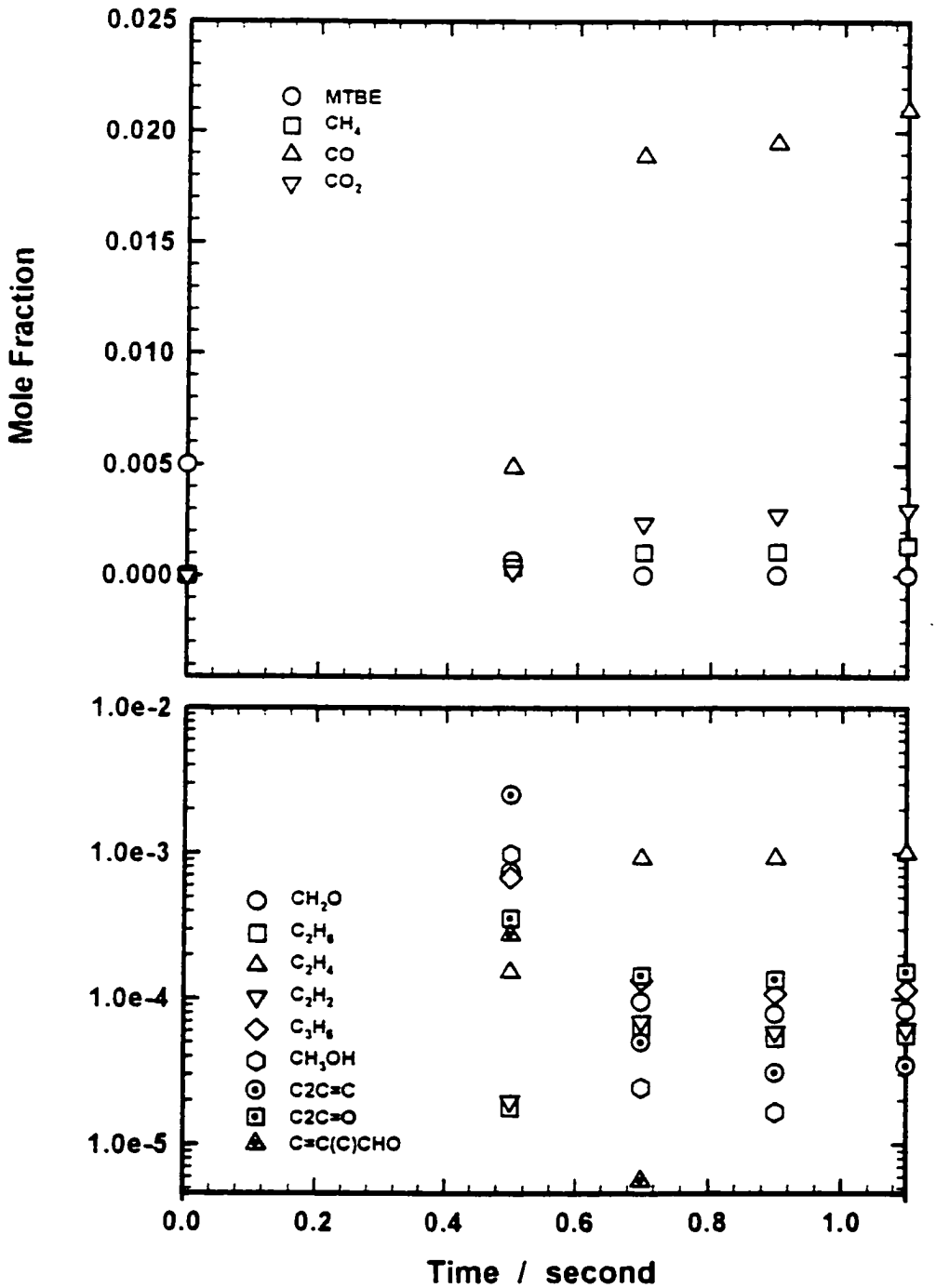


Figure IIC. 9 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 4 atm, T = 898 K

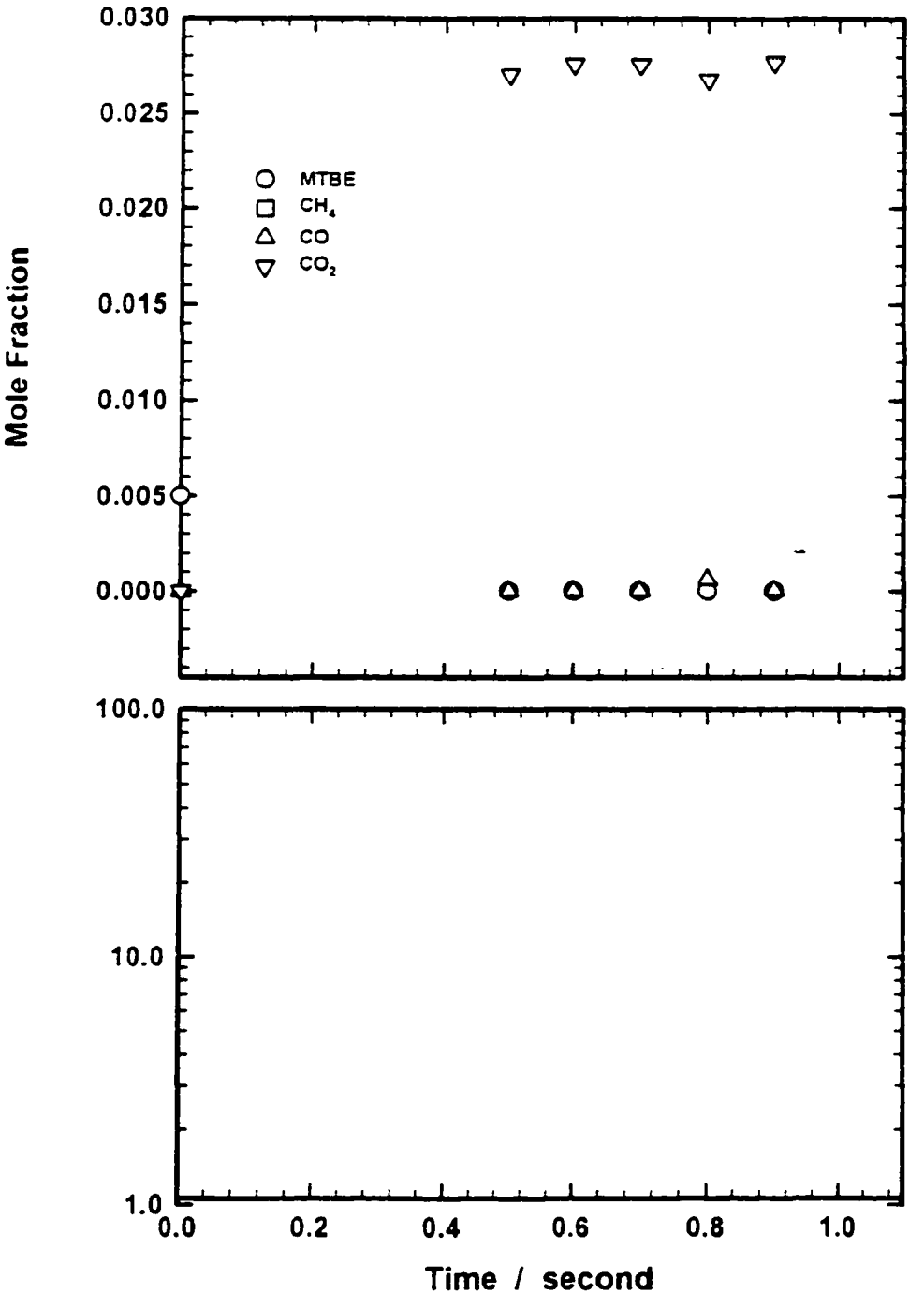


Figure IIC. 10 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 4 atm, T = 923 K

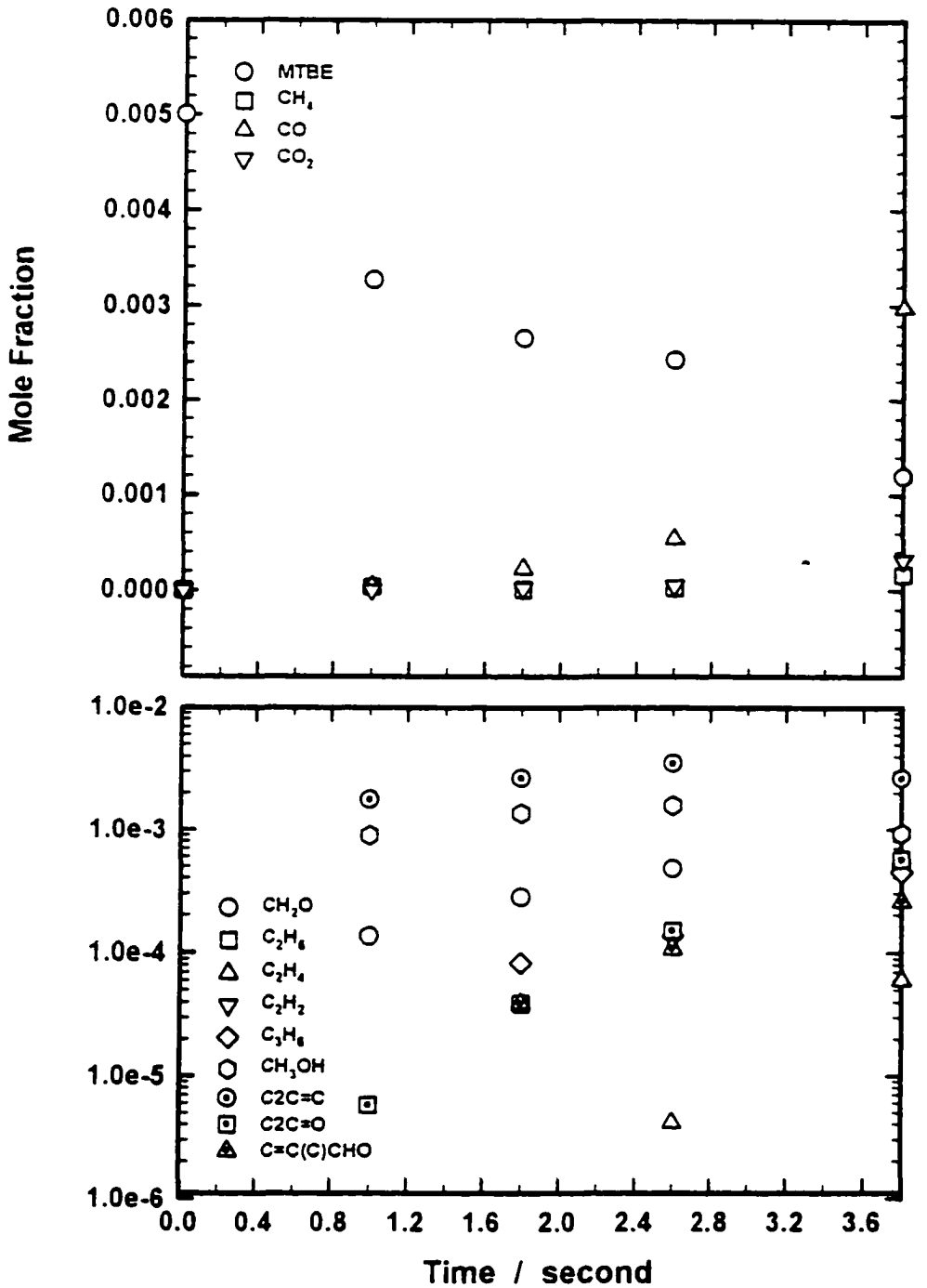


Figure IIC. 11 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 7 atm, T = 798 K

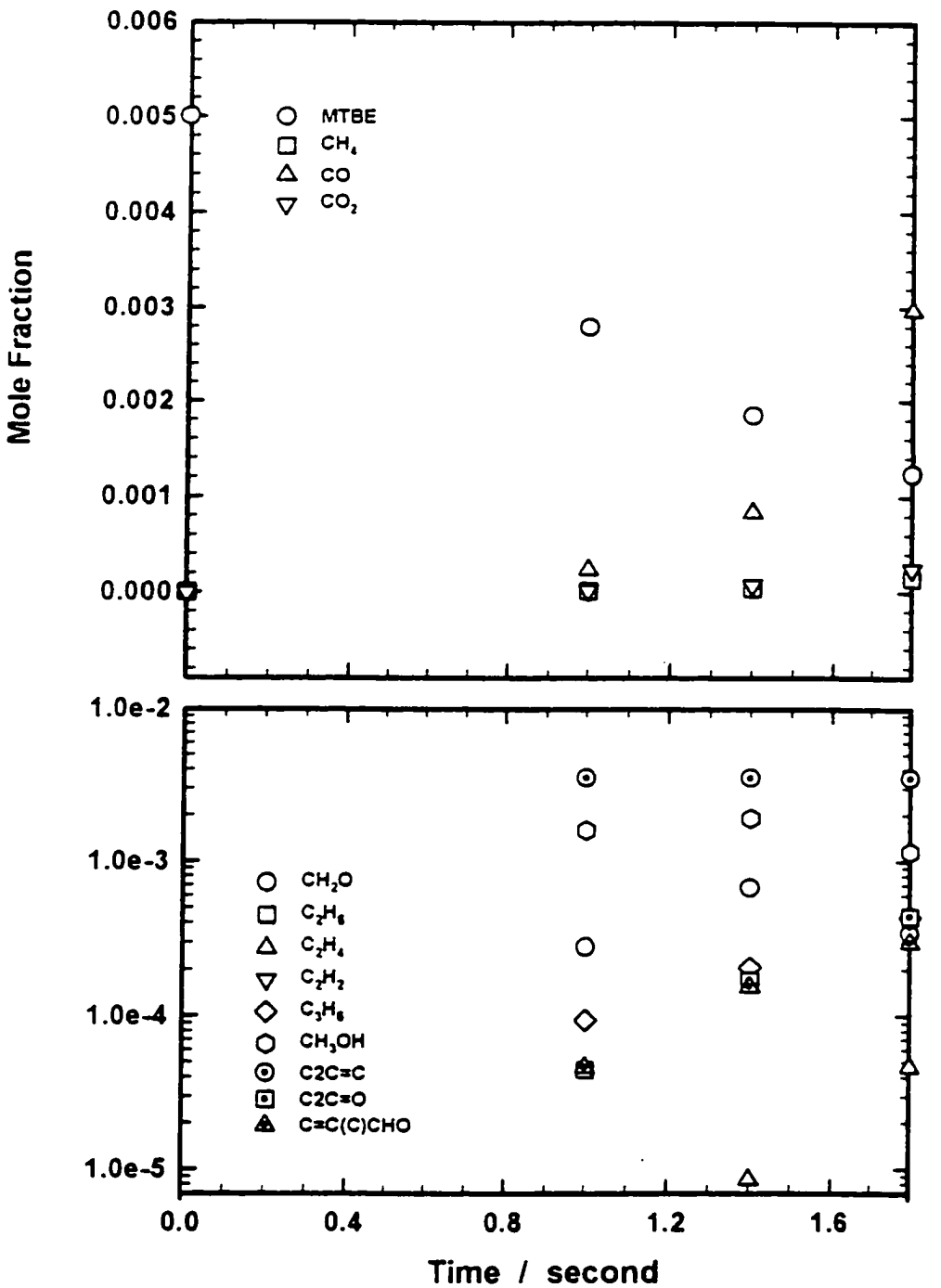


Figure IIC. 12 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 7 atm, T = 823 K

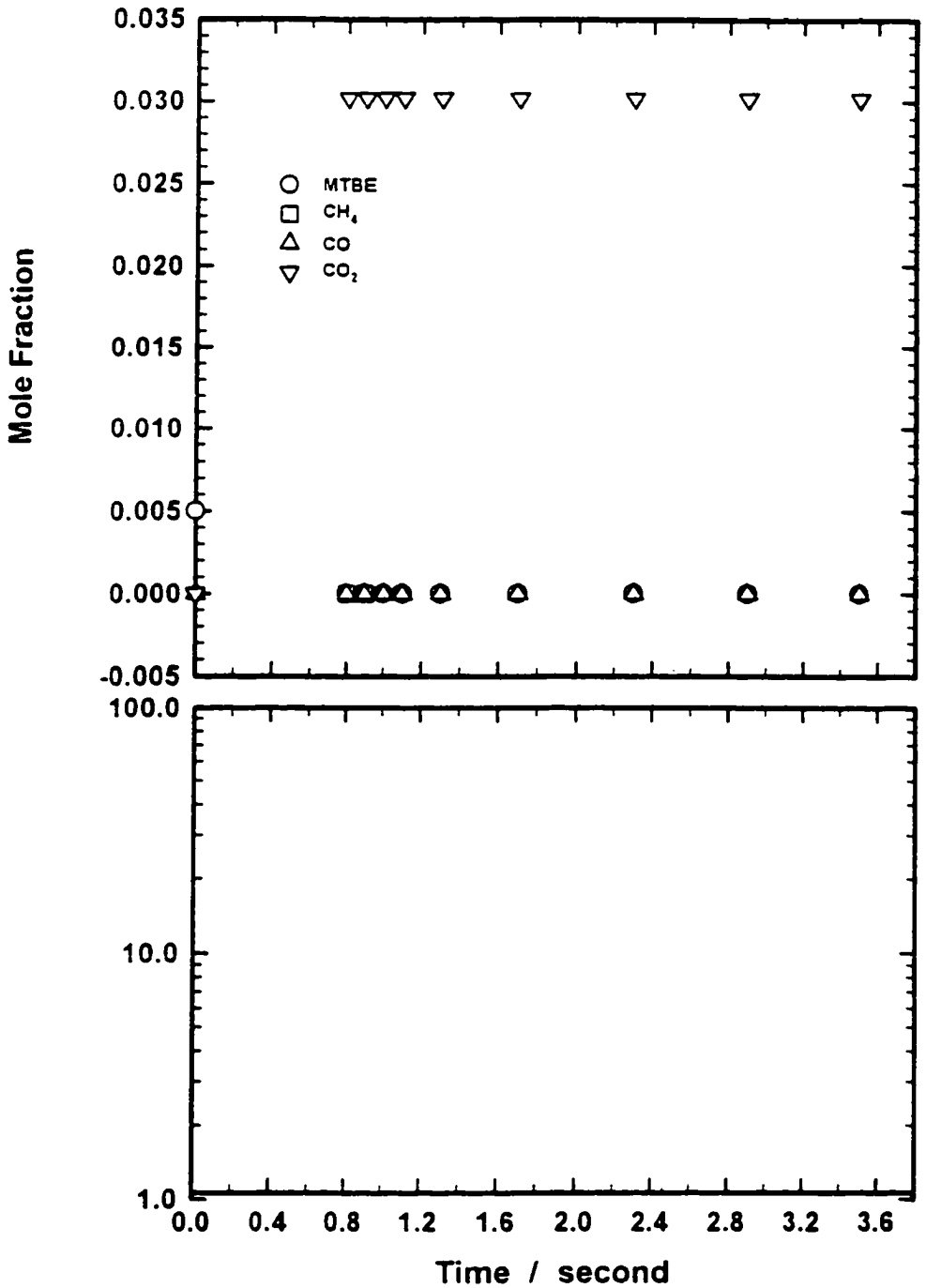


Figure IIC. 13 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 7 atm, T = 873 K

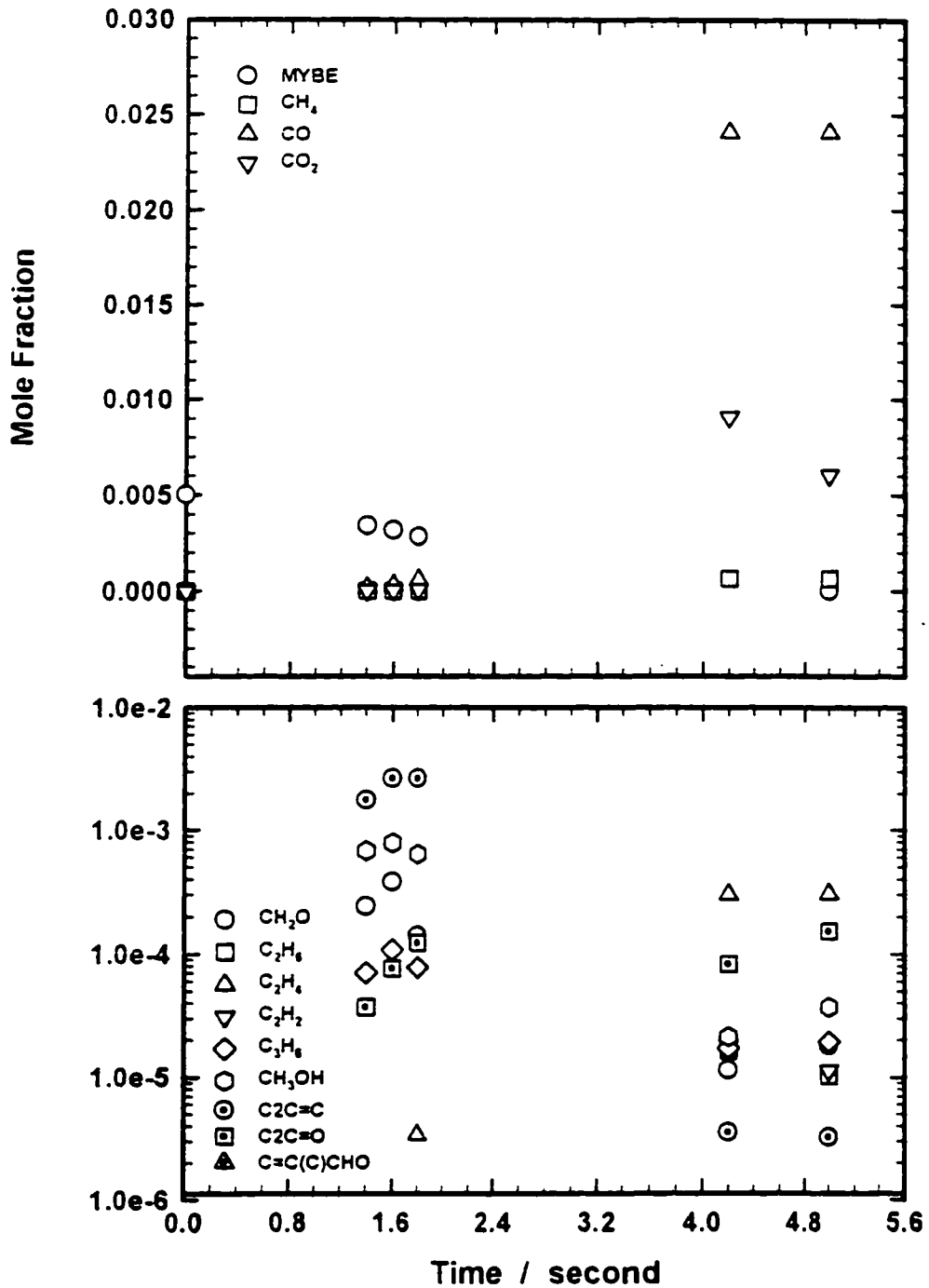


Figure IIC. 14 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 10 atm, T = 798 K

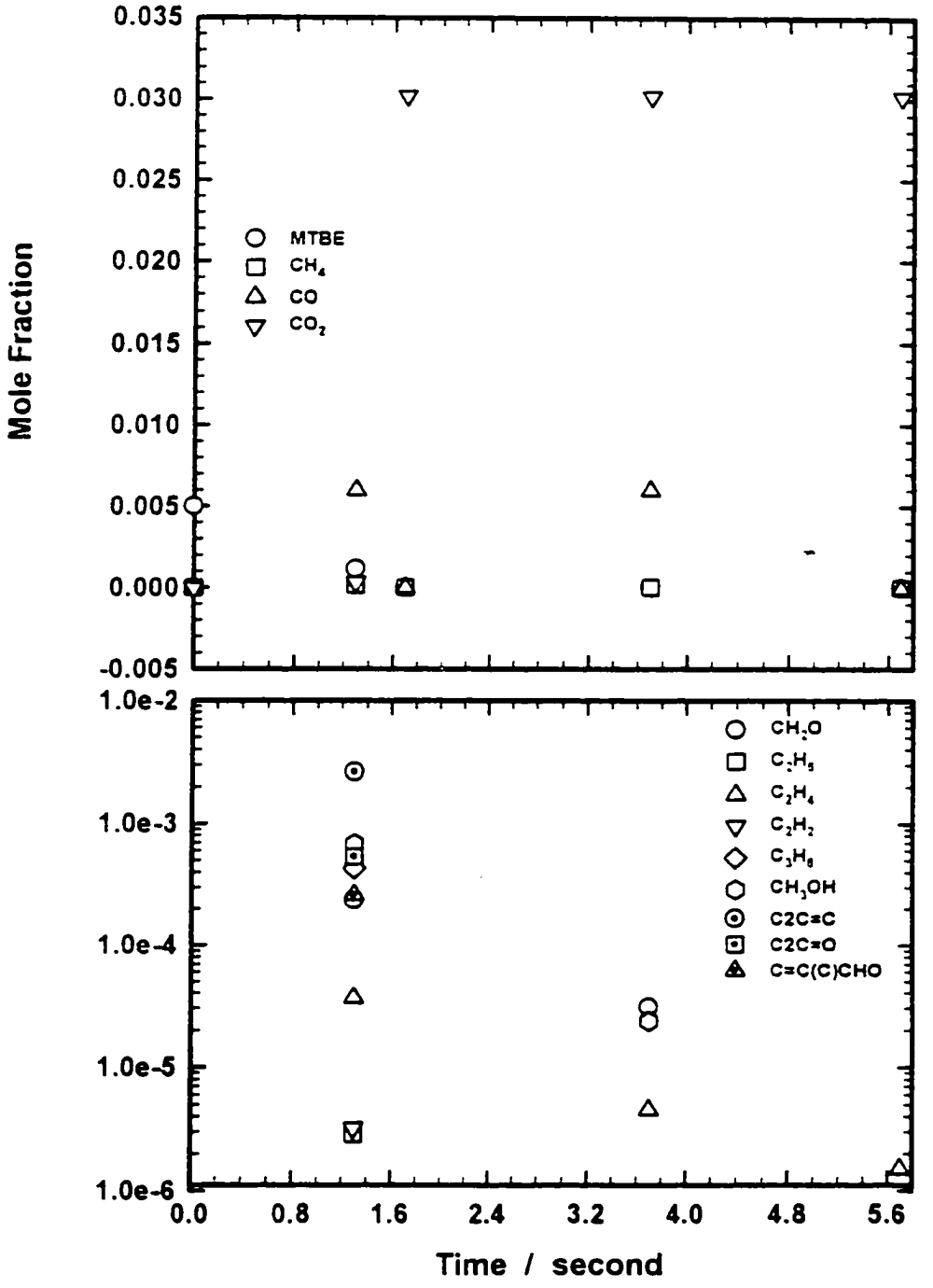


Figure IIC. 15 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 10 atm, T = 823 K

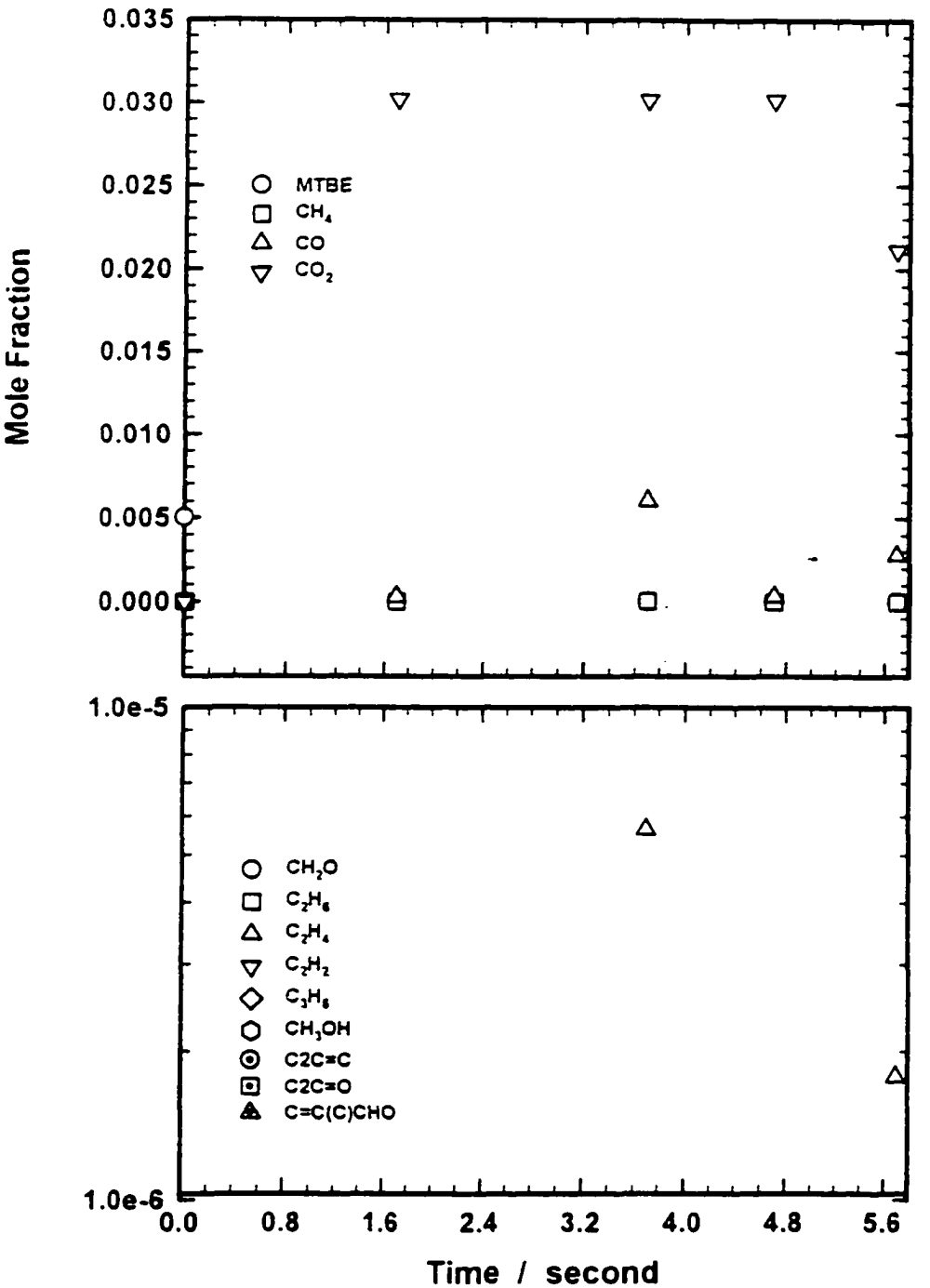


Figure IIC. 16 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 0.75$, P = 10 atm, T = 873 K

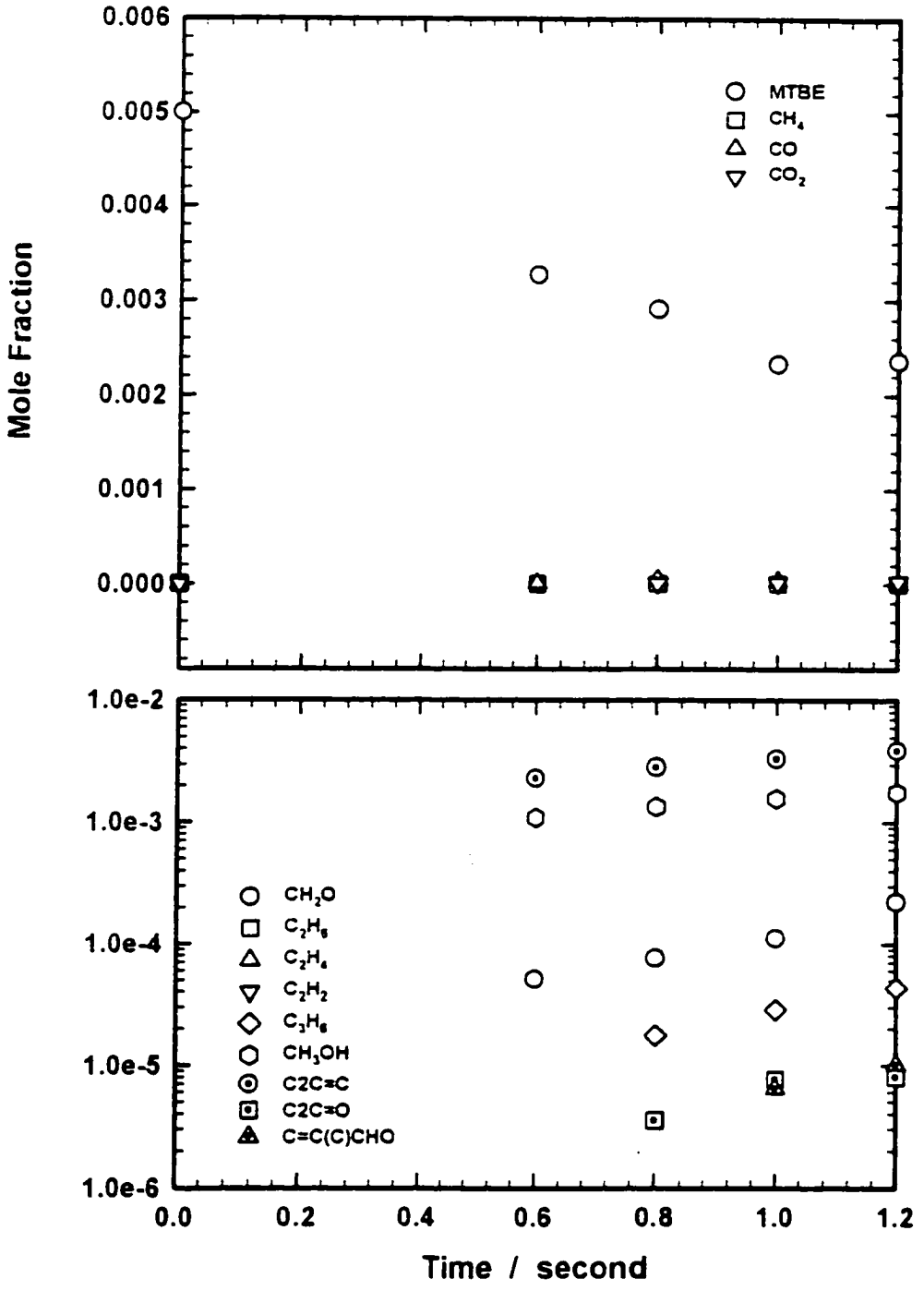


Figure IIC. 17 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 4 atm, T = 823 K

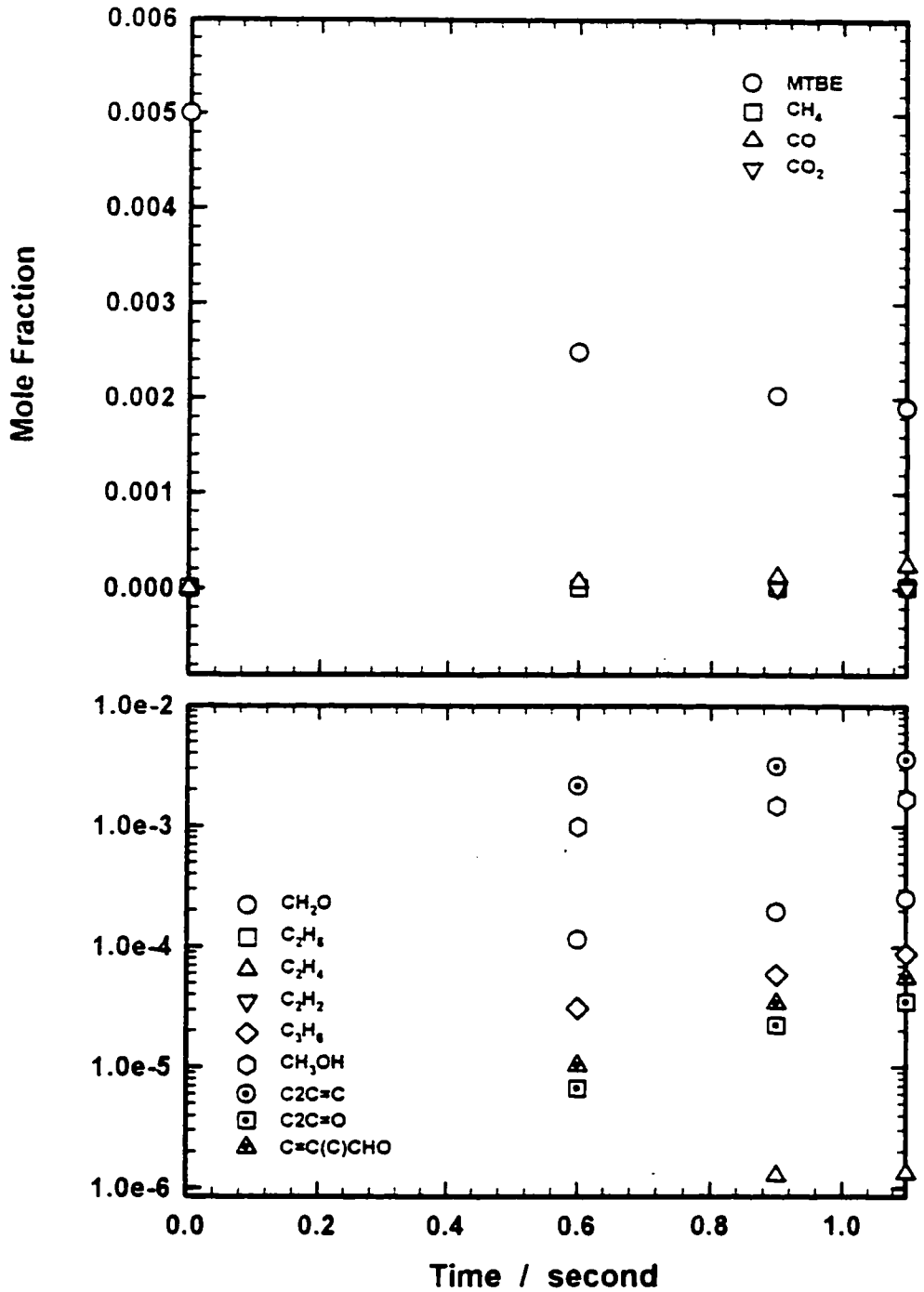


Figure IIC. 18 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 4 atm, T = 848 K

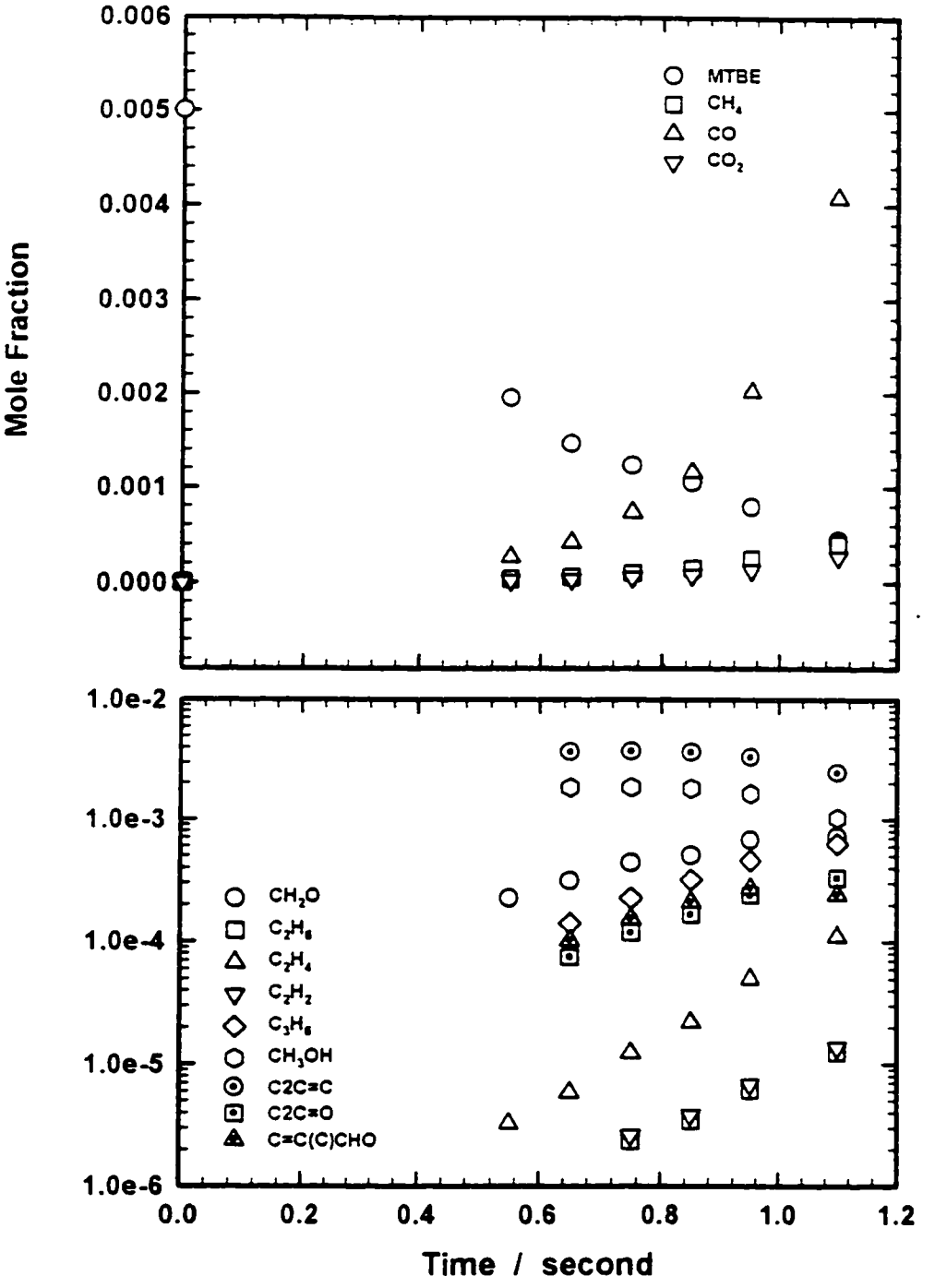


Figure IIC. 19 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 4 atm, T = 873 K

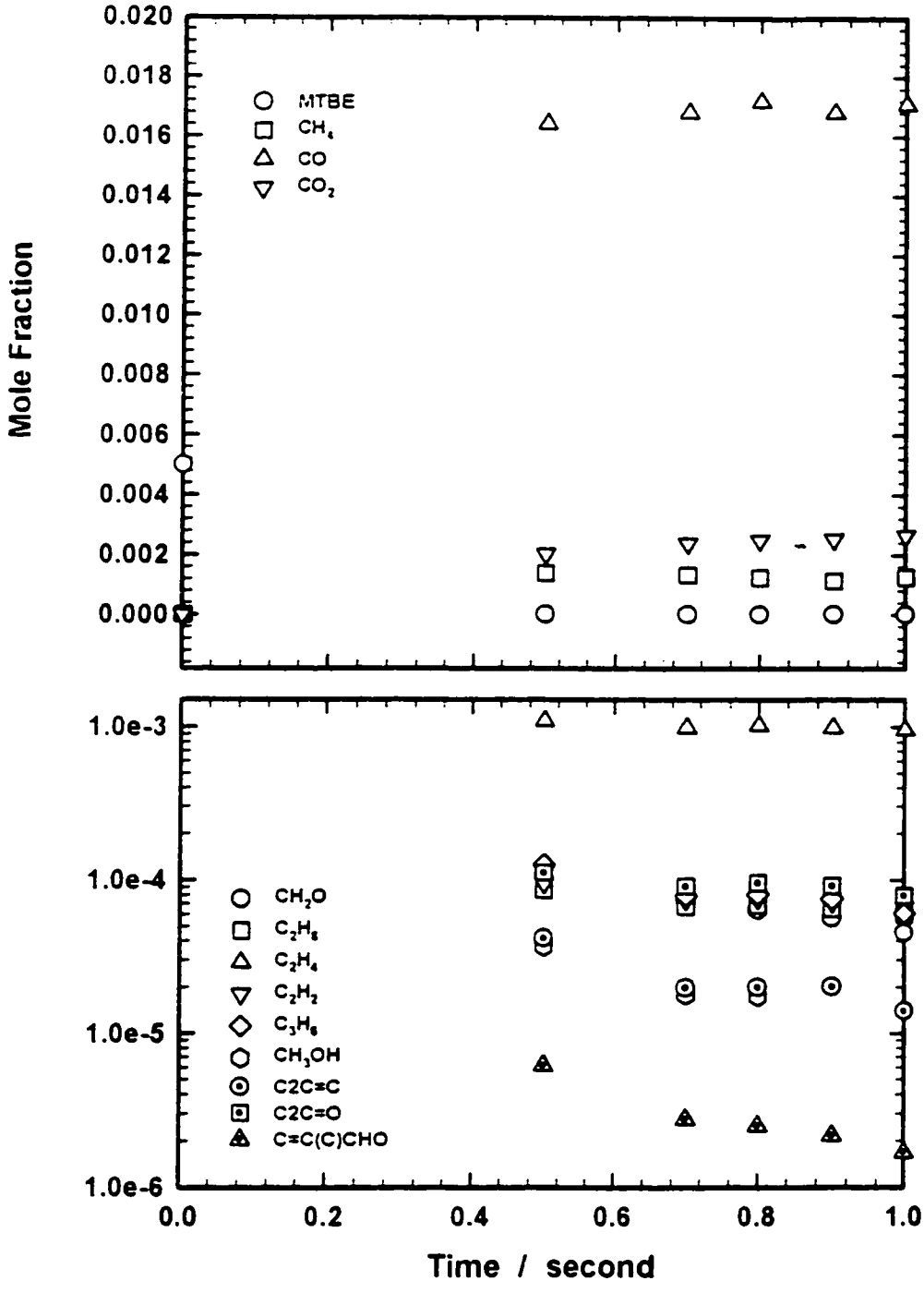


Figure IIC. 20 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 4 atm, T = 923 K

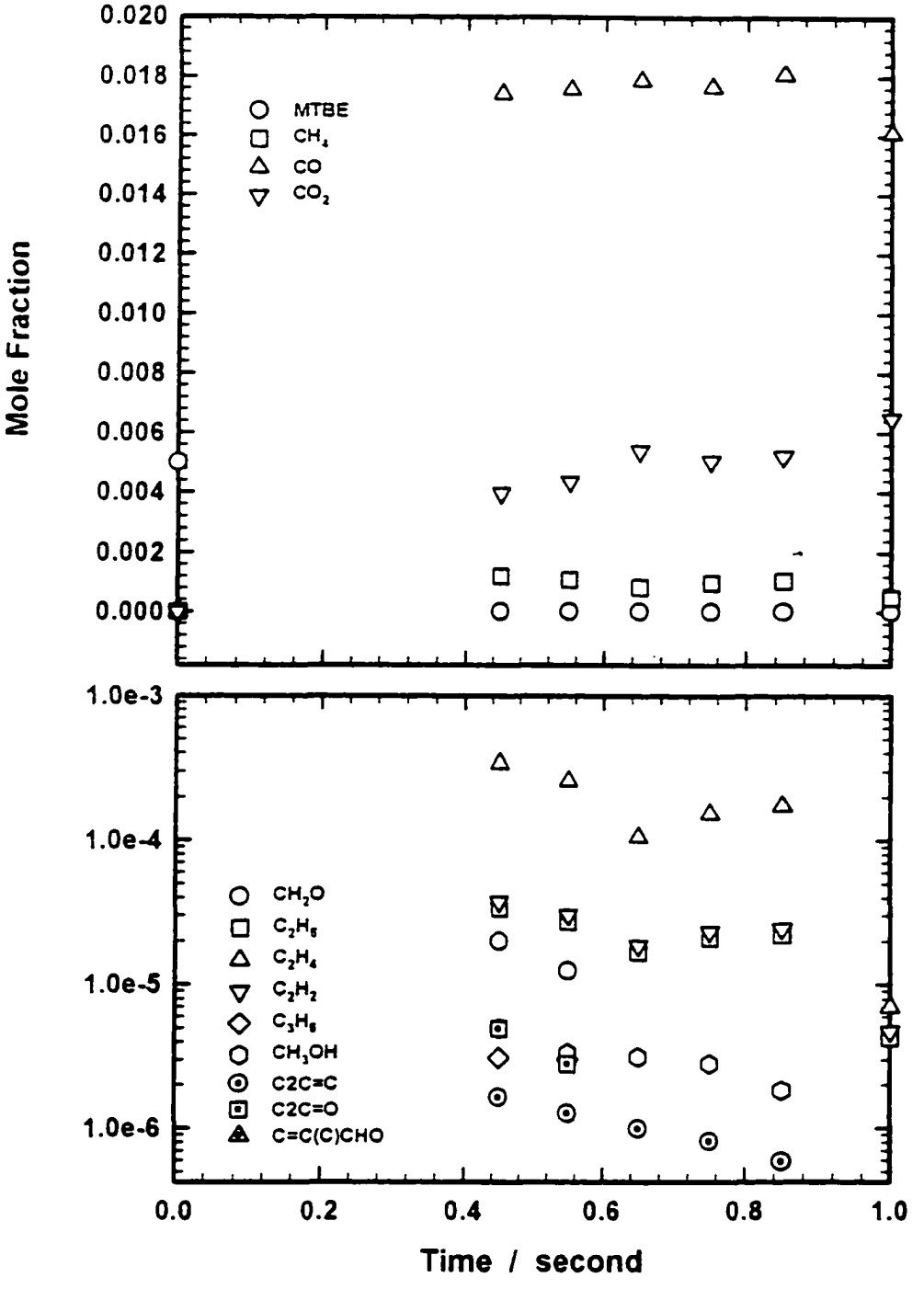


Figure IIC. 21 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 4 atm, T = 973 K

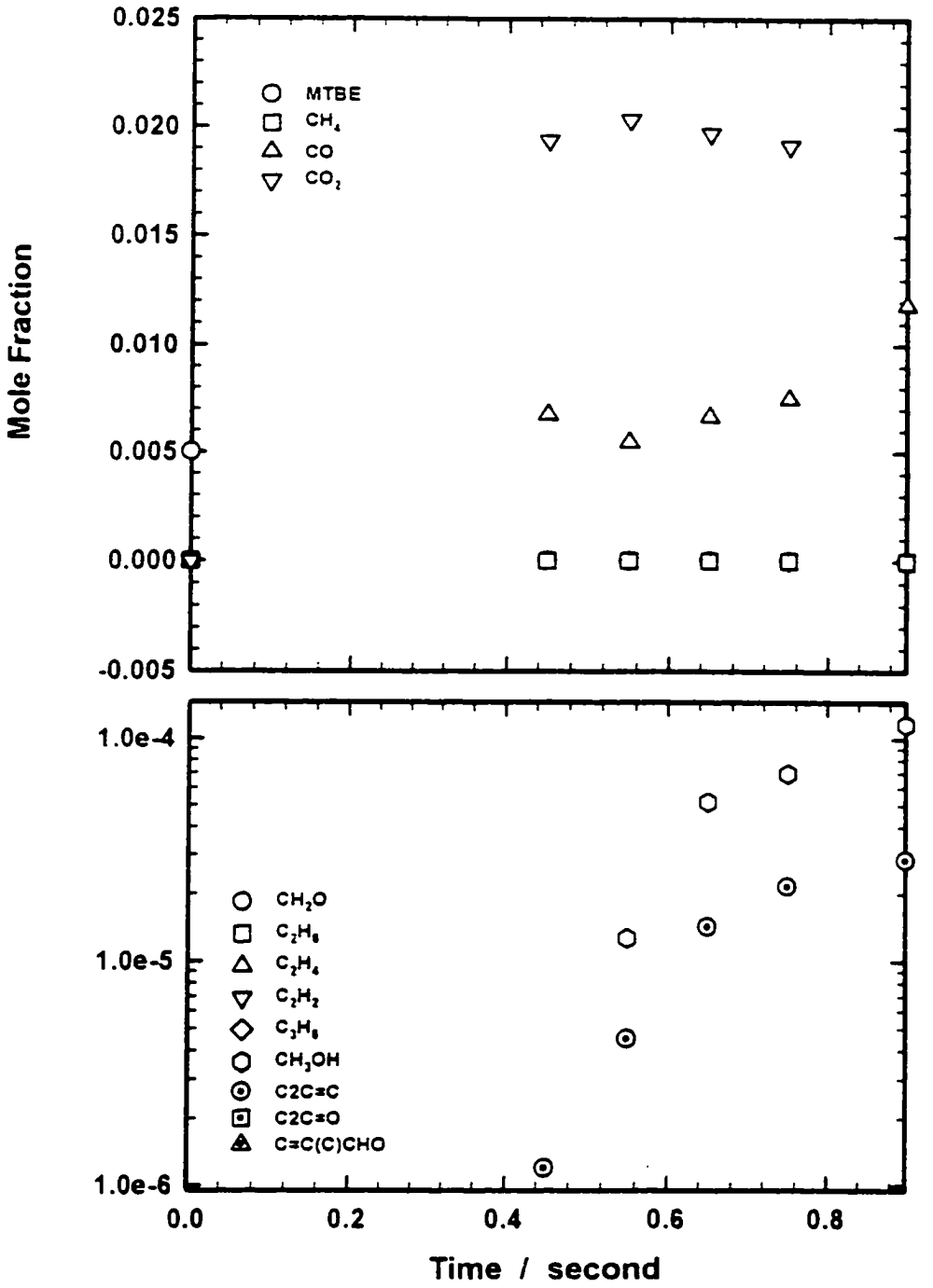


Figure IIC. 22 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 4 atm, T = 1023 K

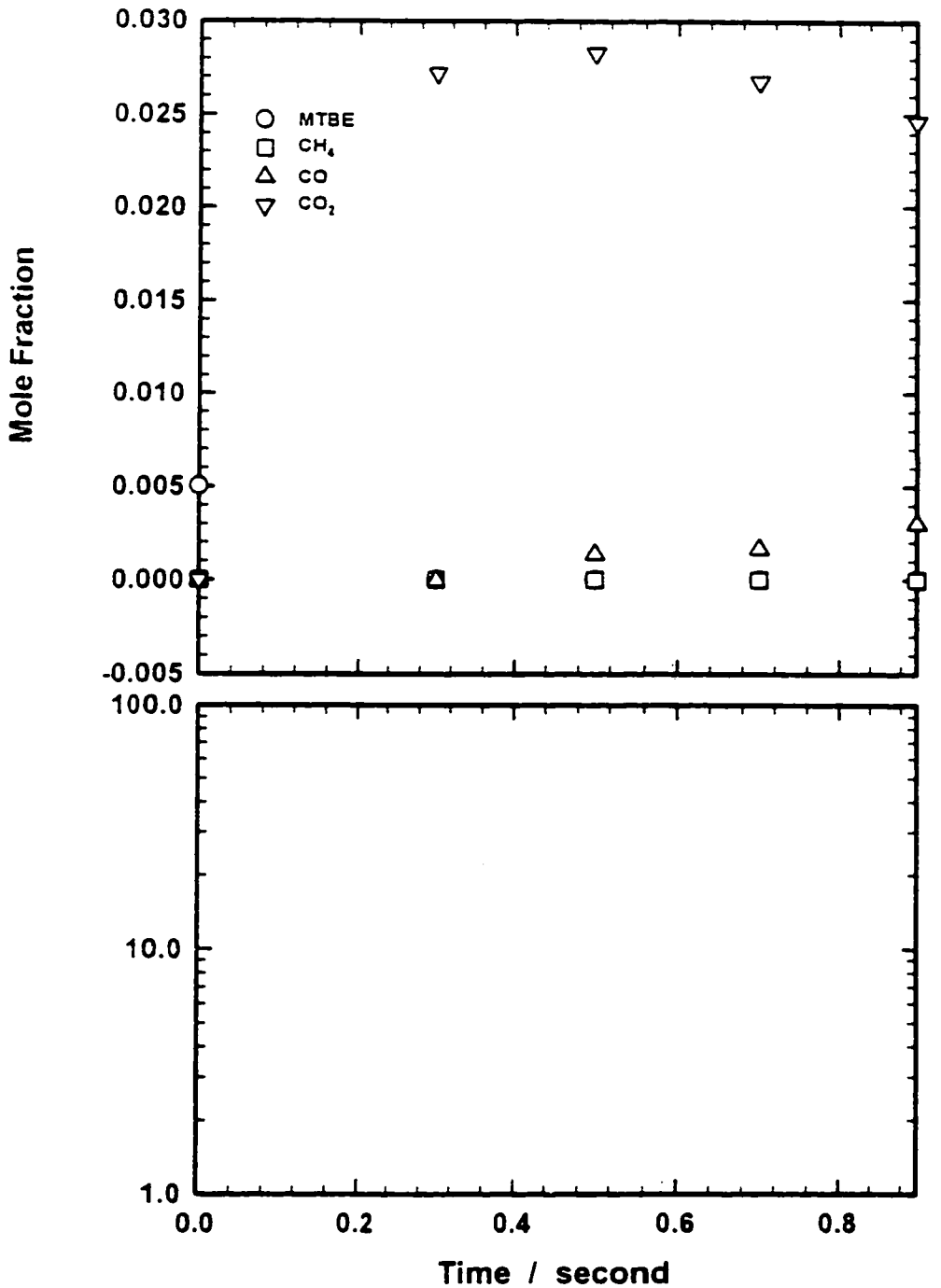


Figure IIC. 23 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 4 atm, T = 1073 K

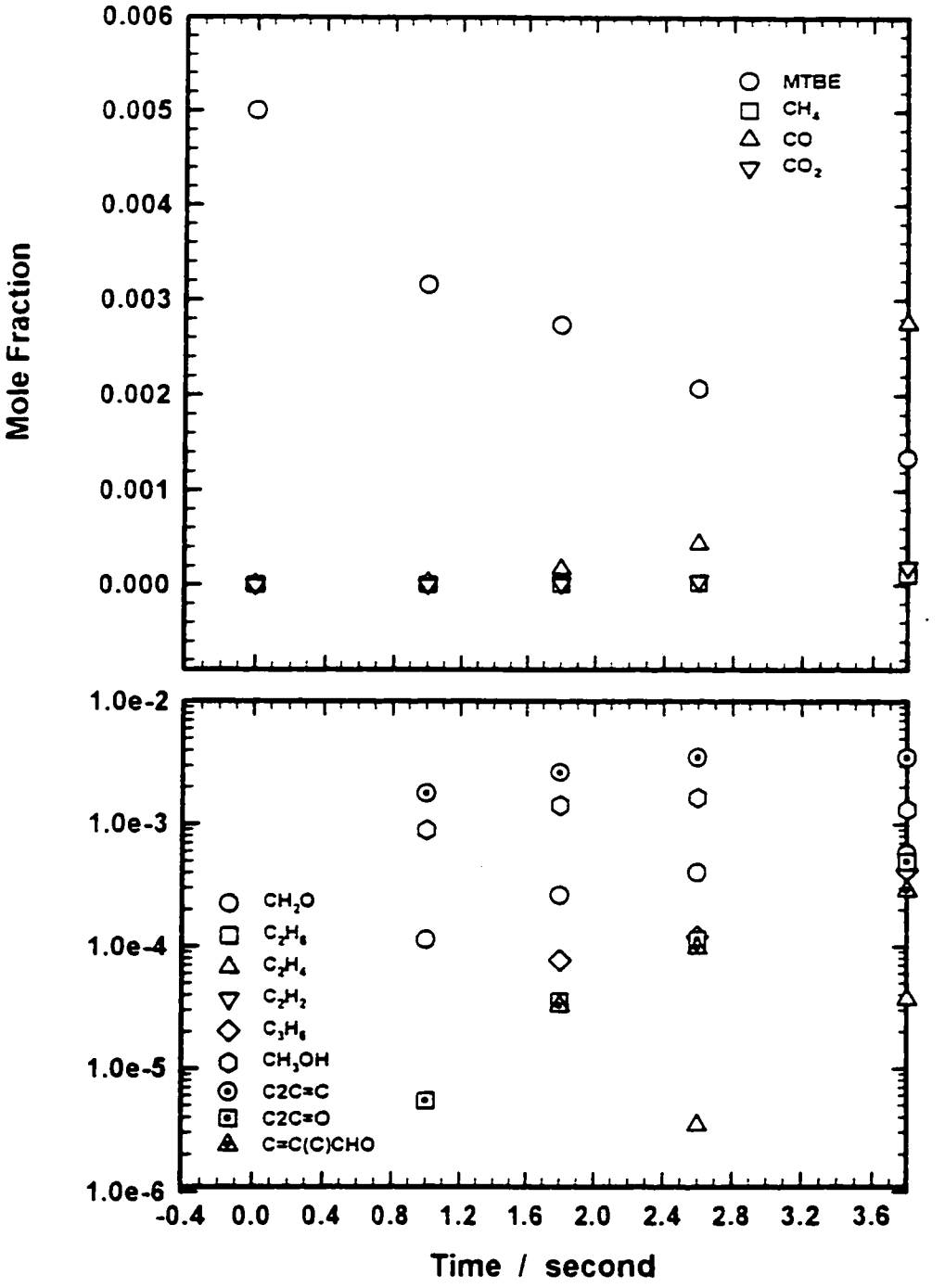


Figure IIC. 24 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P =7 atm, T = 798 K

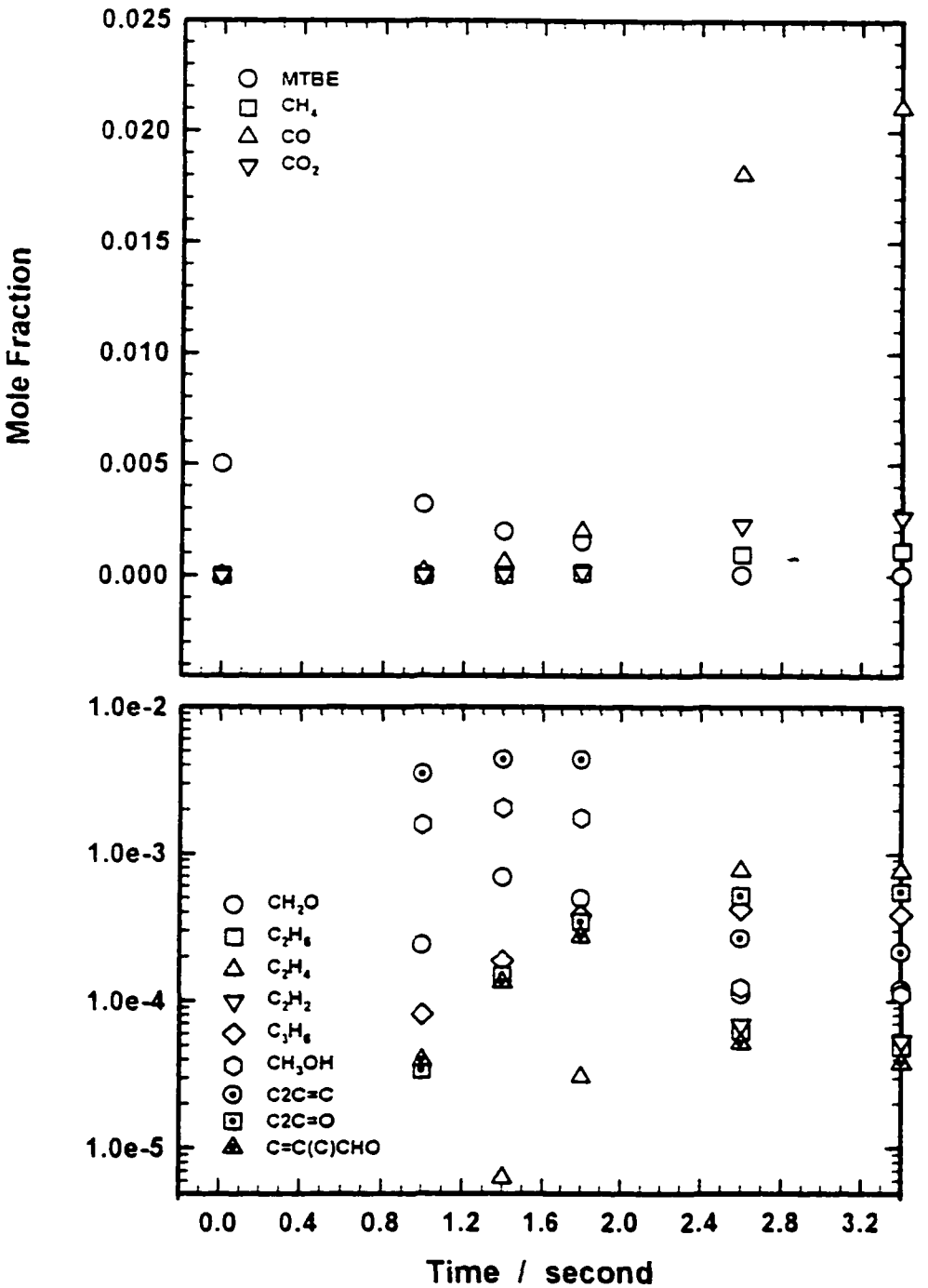


Figure IIC. 25 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P =7 atm, T = 823 K

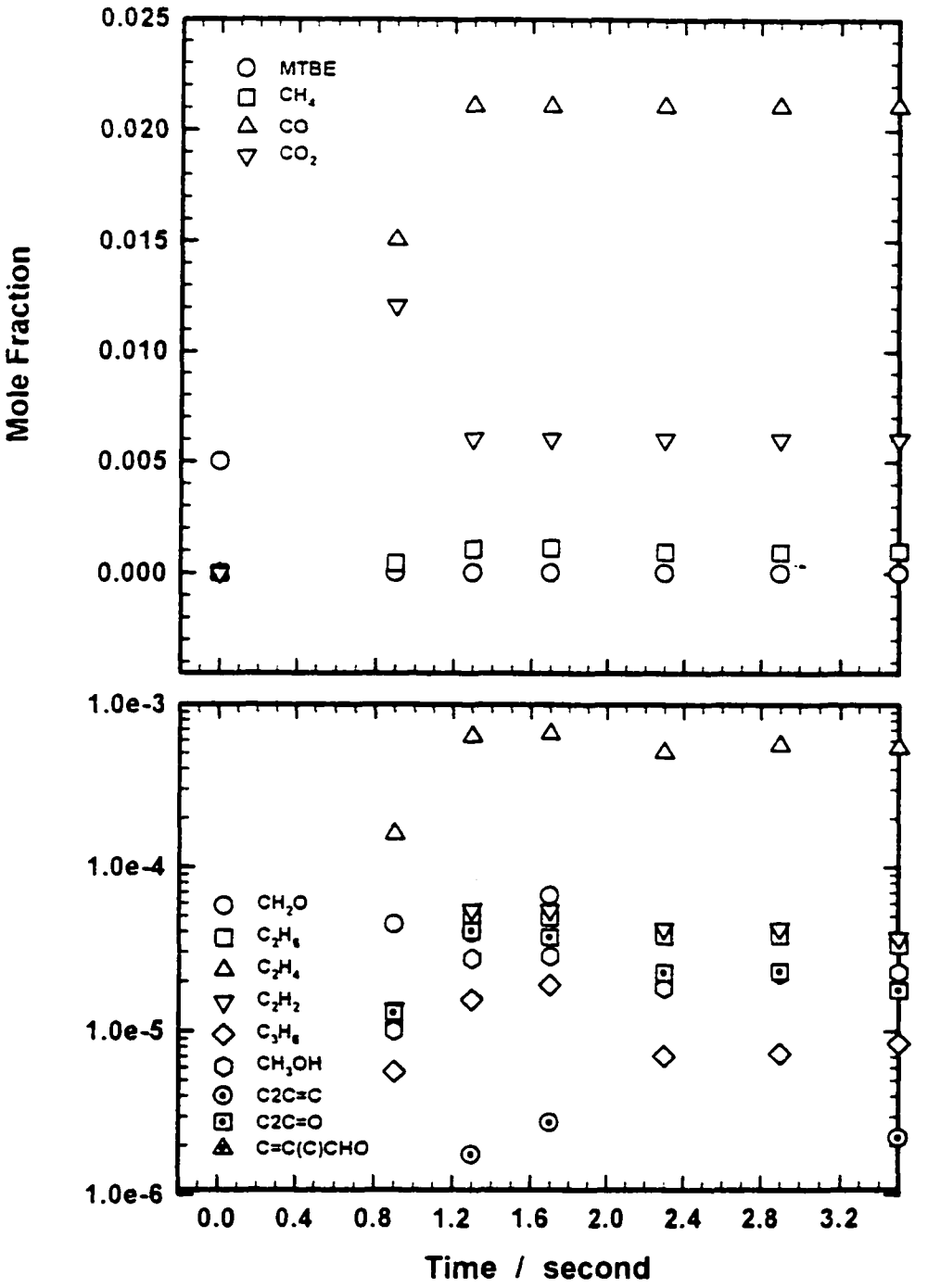


Figure IIC. 26 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P =7 atm, T = 873 K

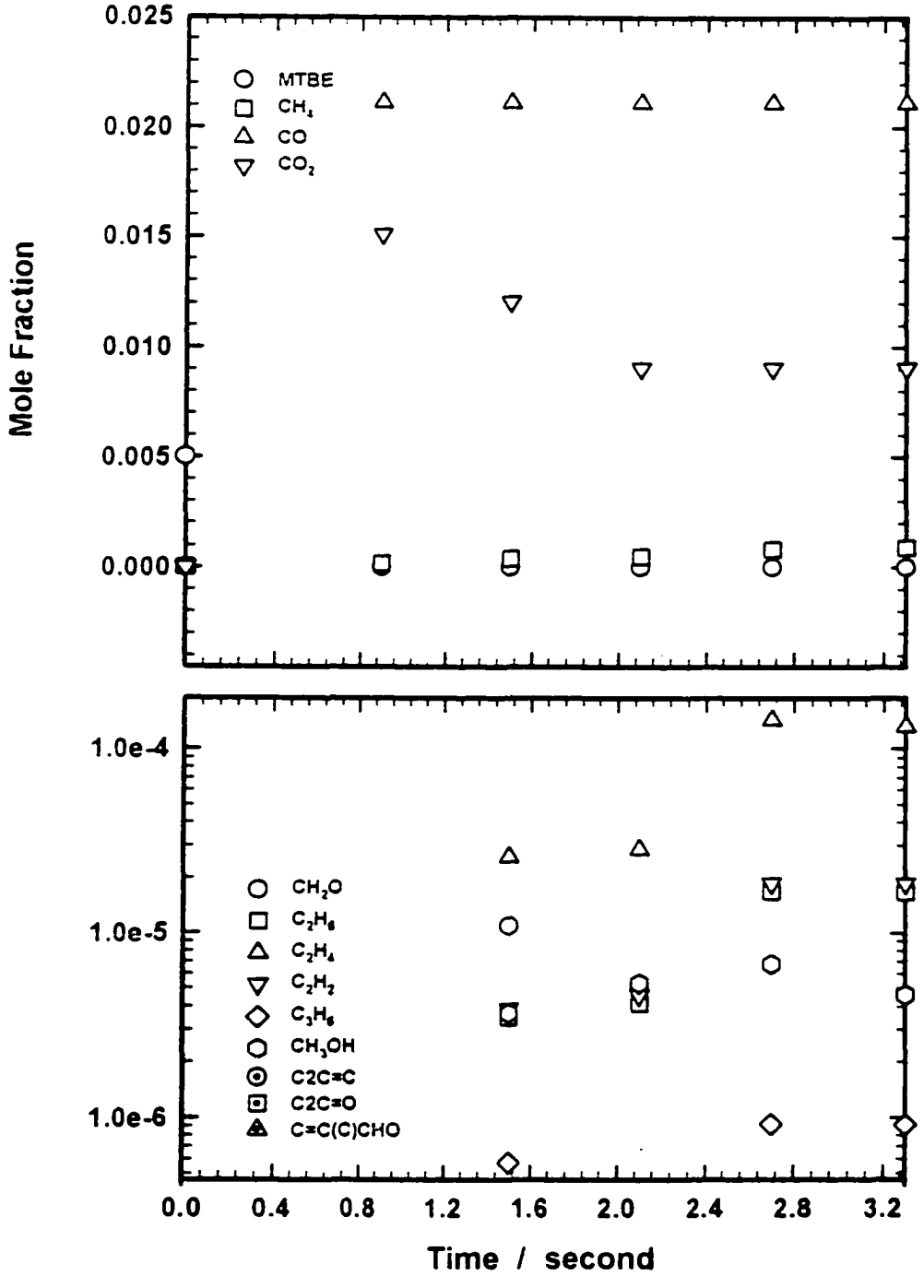


Figure IIC. 27 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P =7 atm, T = 923 K

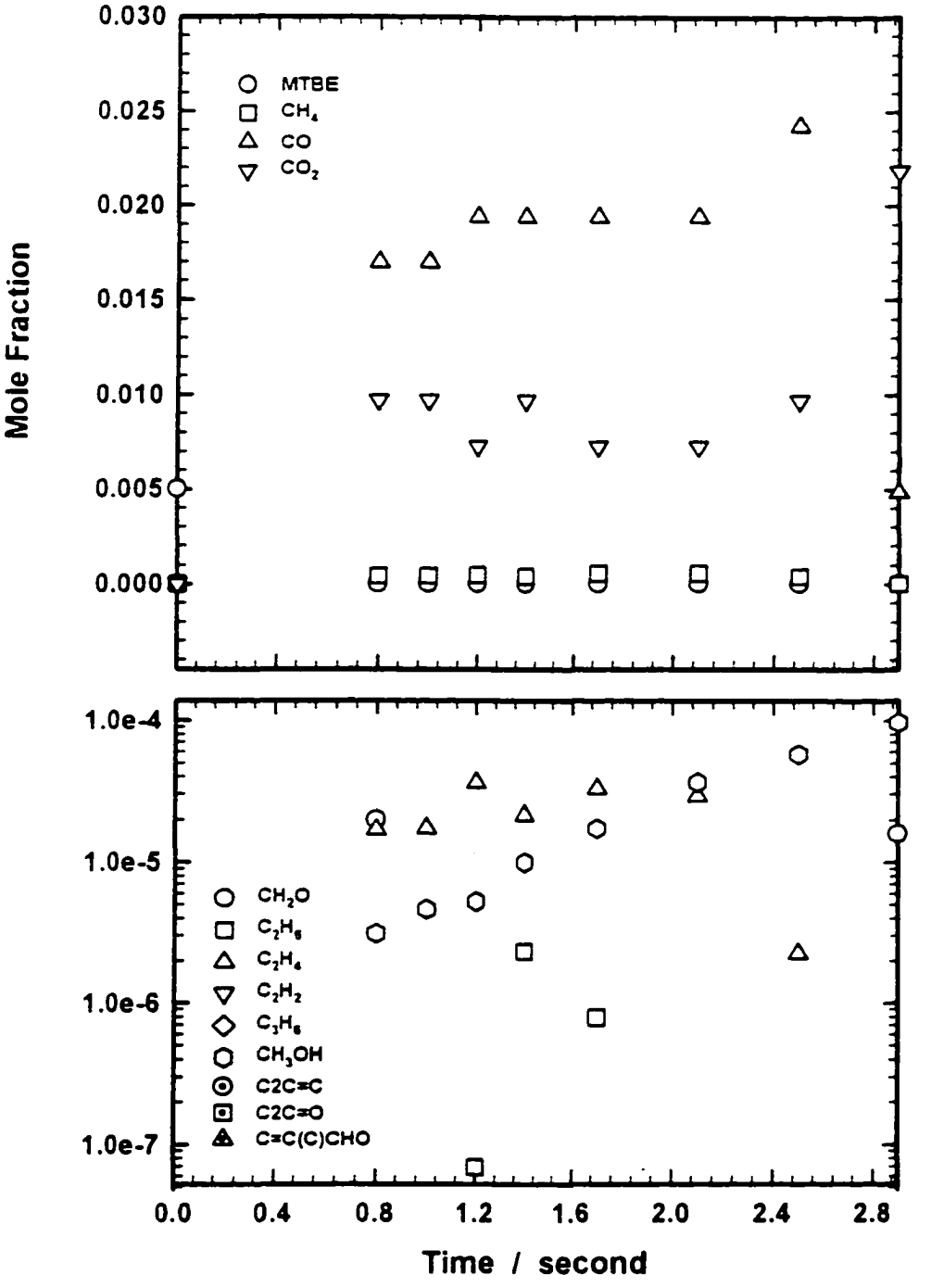


Figure IIC. 28 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P =7 atm, T = 1023 K

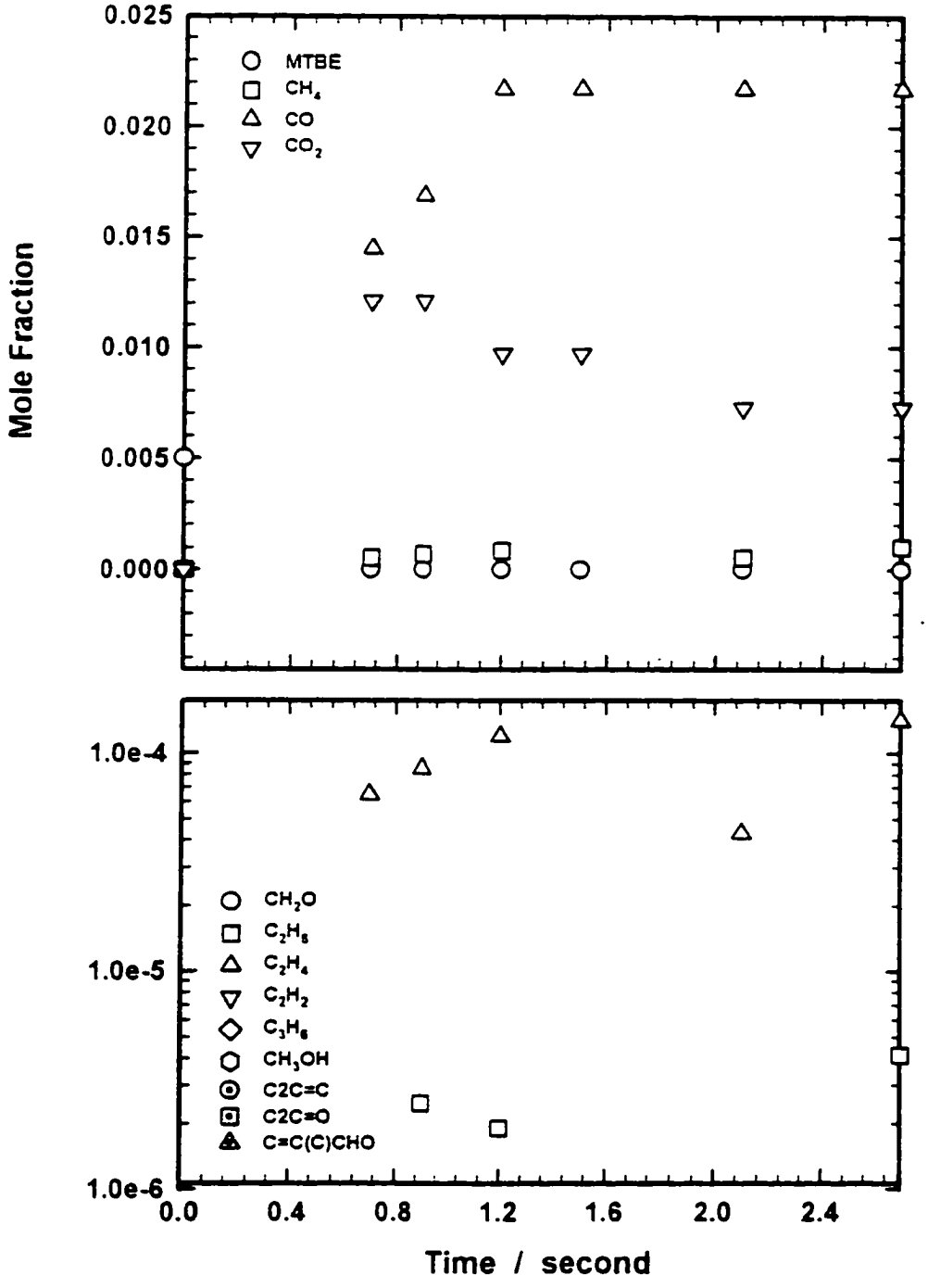


Figure IIC. 29 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P =7 atm, T = 1073 K

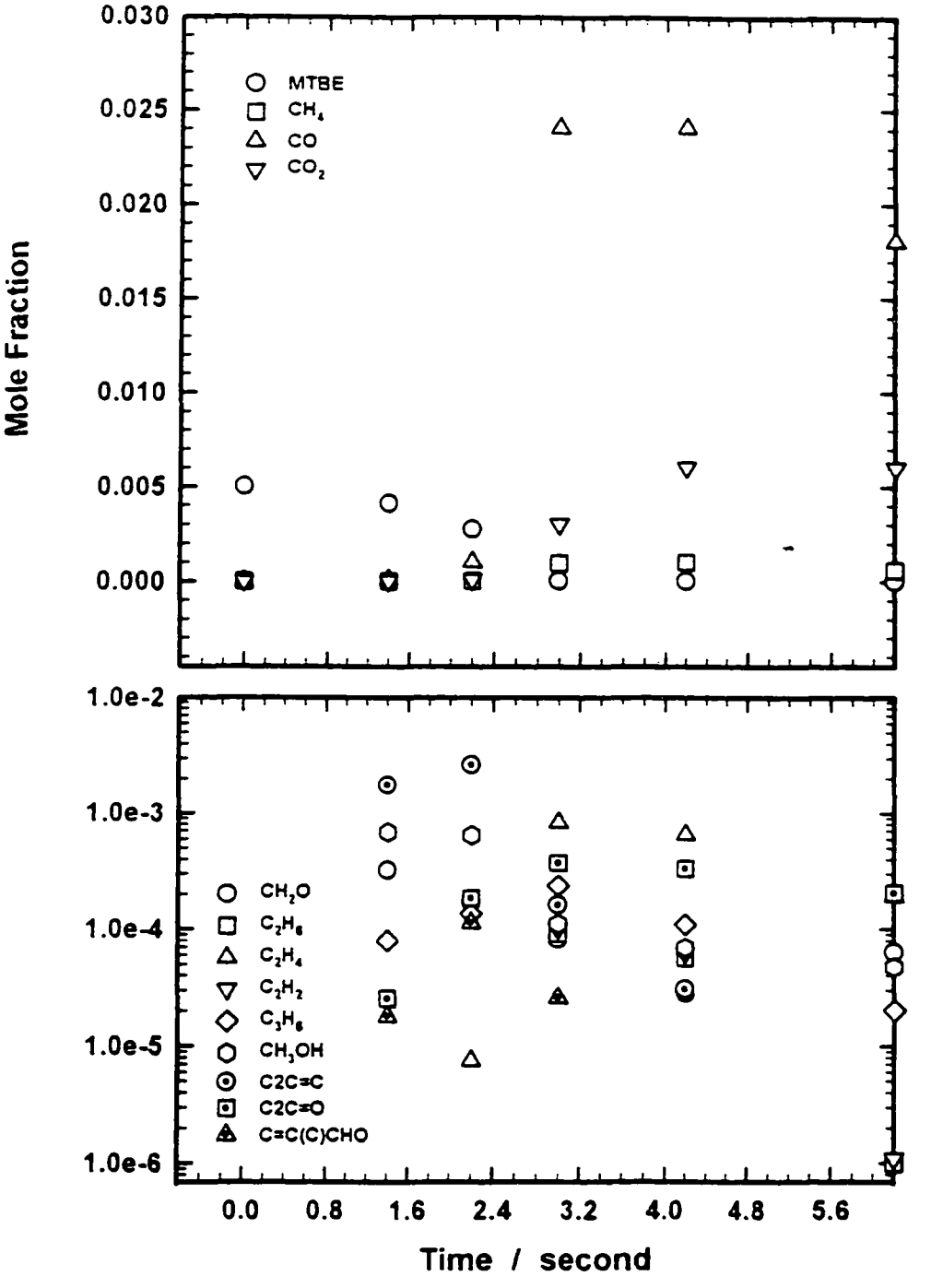


Figure IIC. 30 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 10 atm, T = 798 K

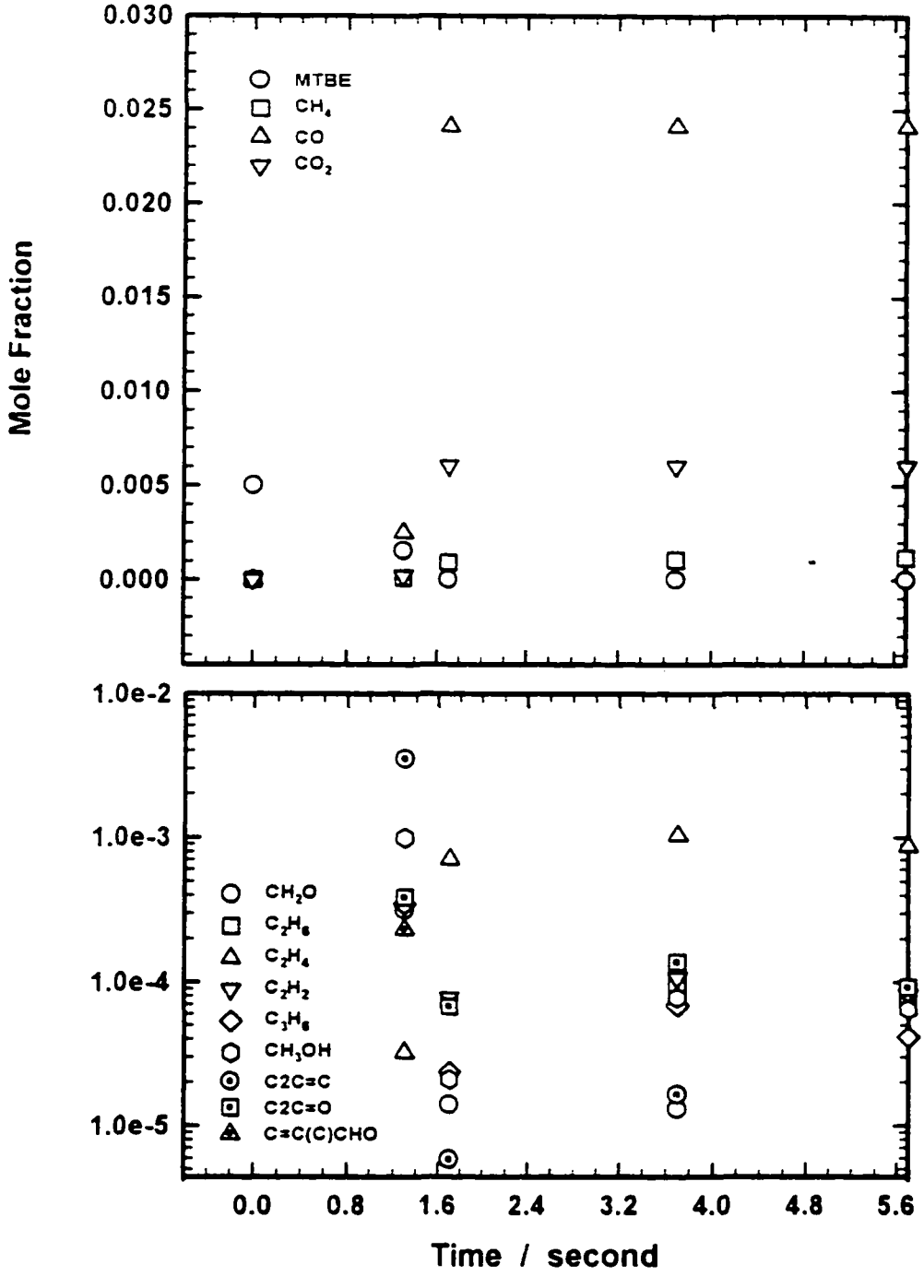


Figure IIC. 31 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 10 atm, T = 823 K

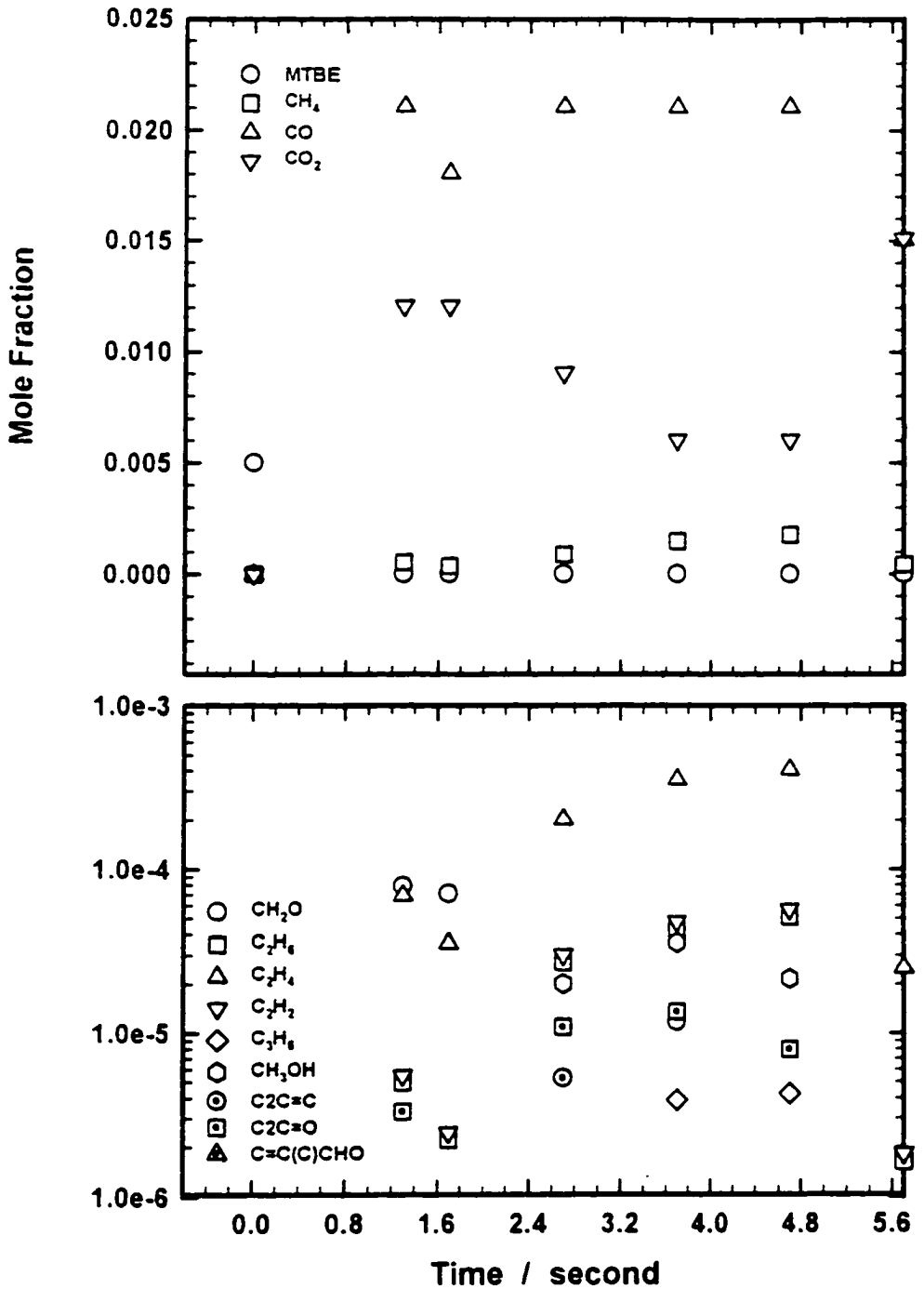


Figure IIC. 32 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 10 atm, T = 873 K

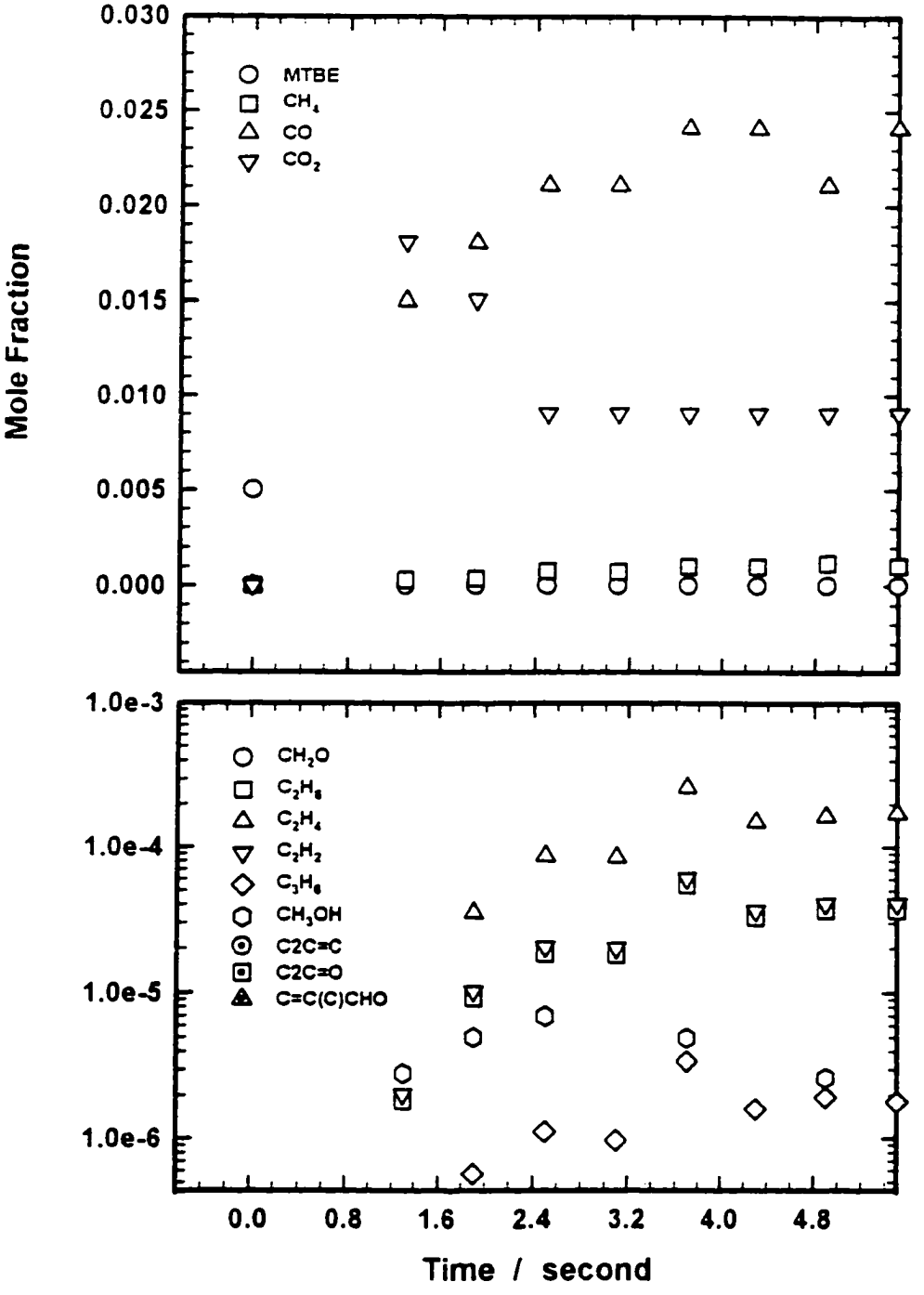


Figure IIC. 33 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 10 atm, T = 923 K

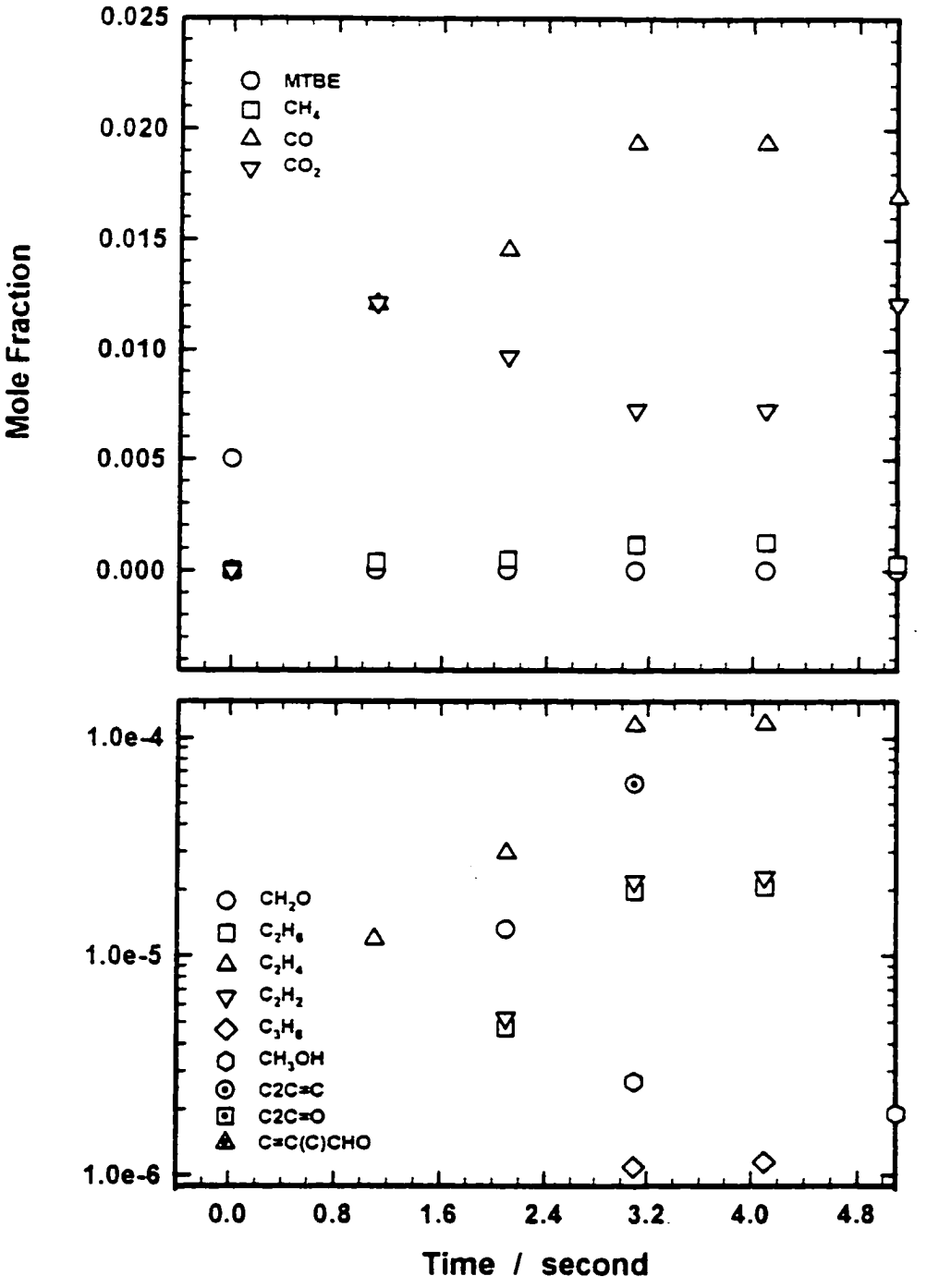


Figure IIC. 34 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 10 atm, T = 973 K

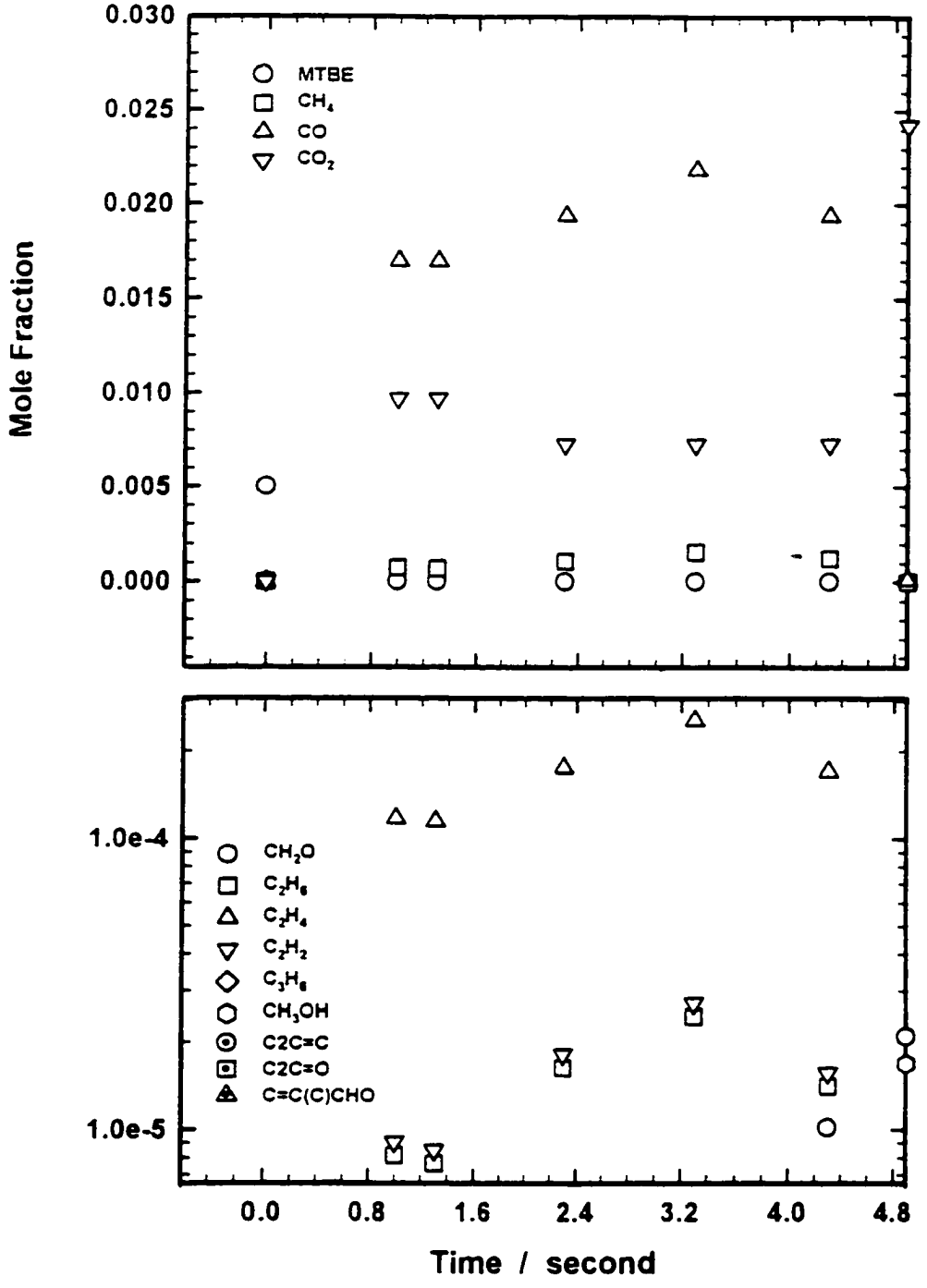


Figure IIC. 35 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 10 atm, T = 1023 K

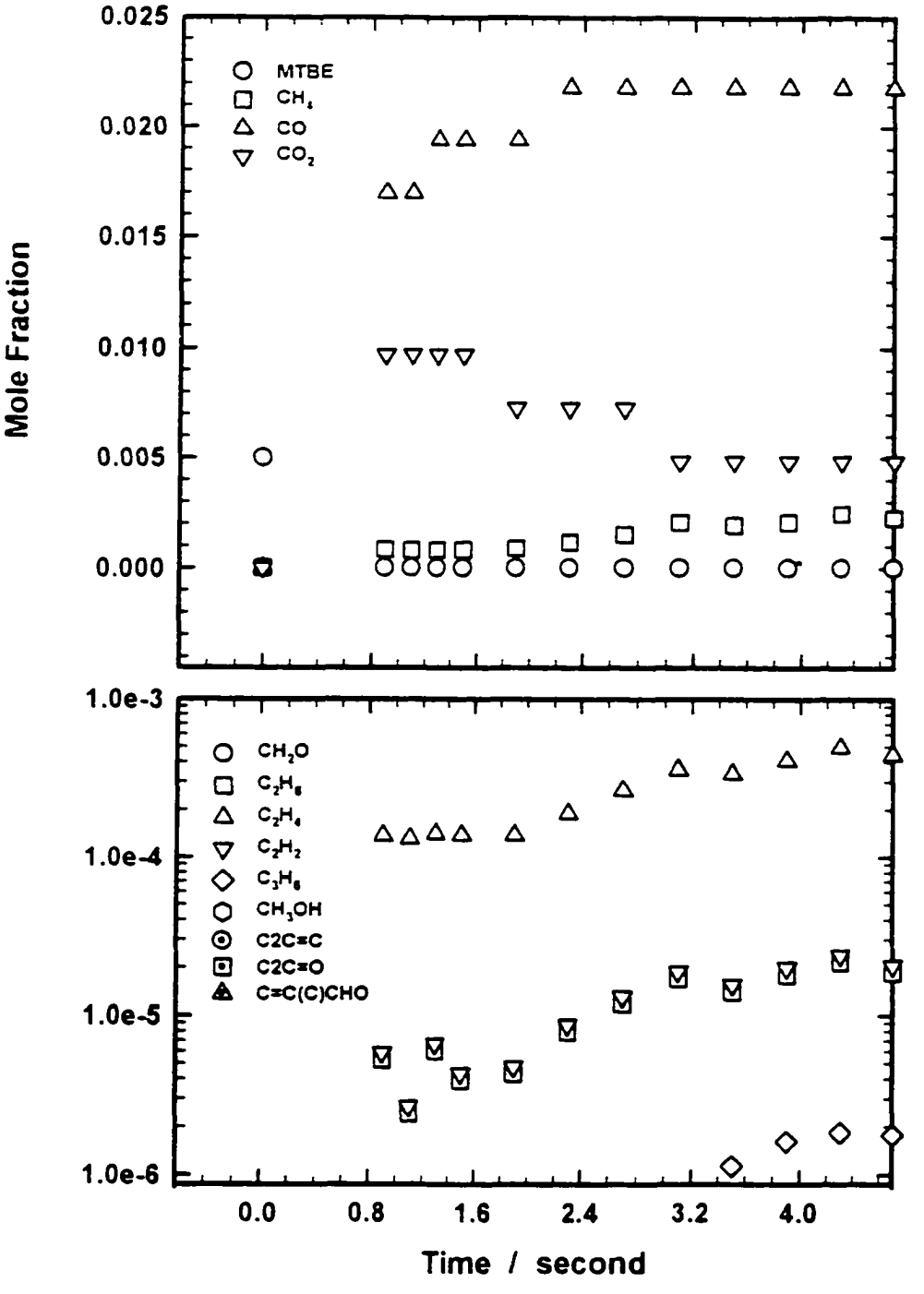


Figure IIC. 36 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.00, P = 10 atm, T = 1073 K

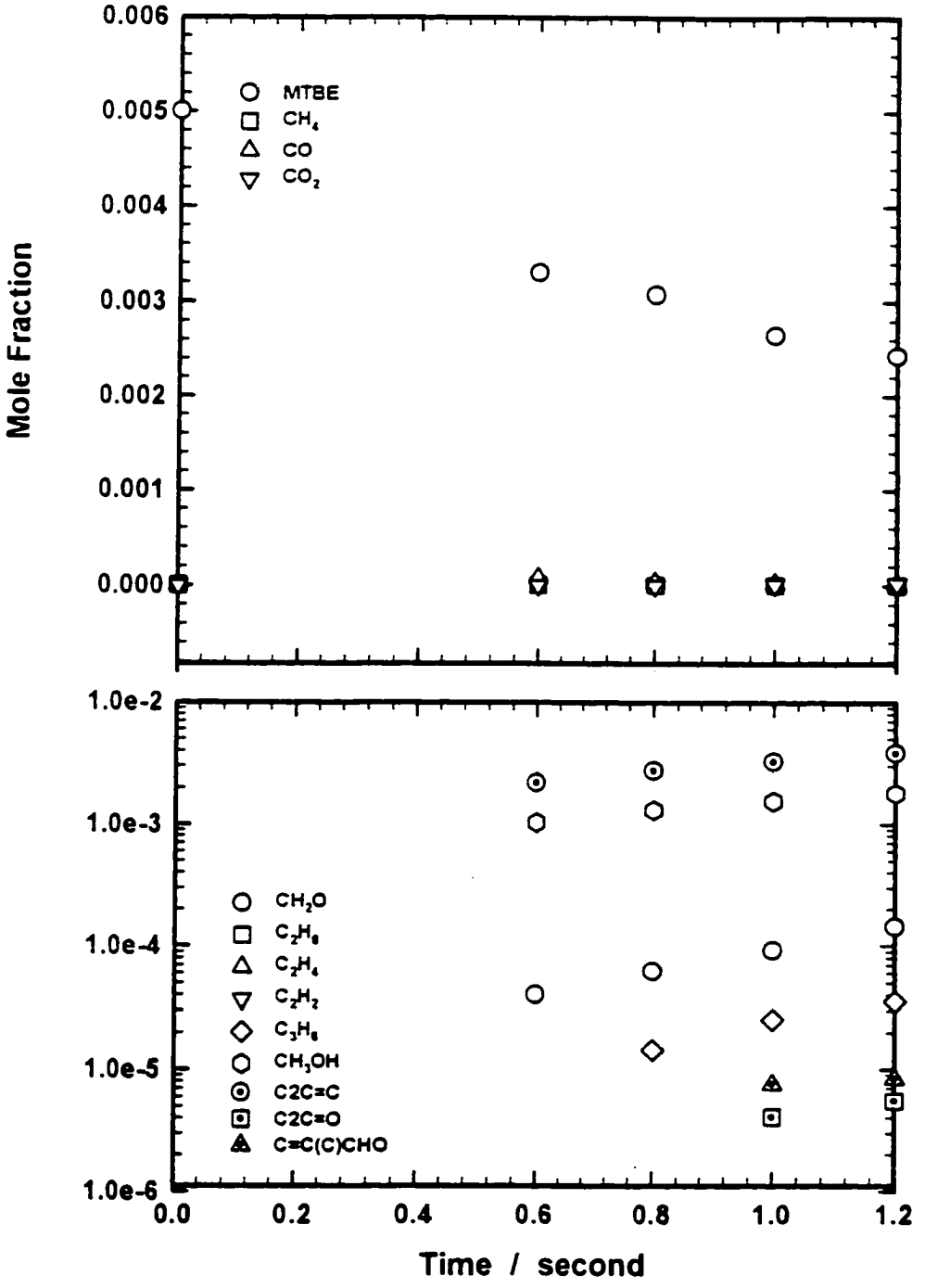


Figure IIC. 37 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 4 atm, T = 823 K

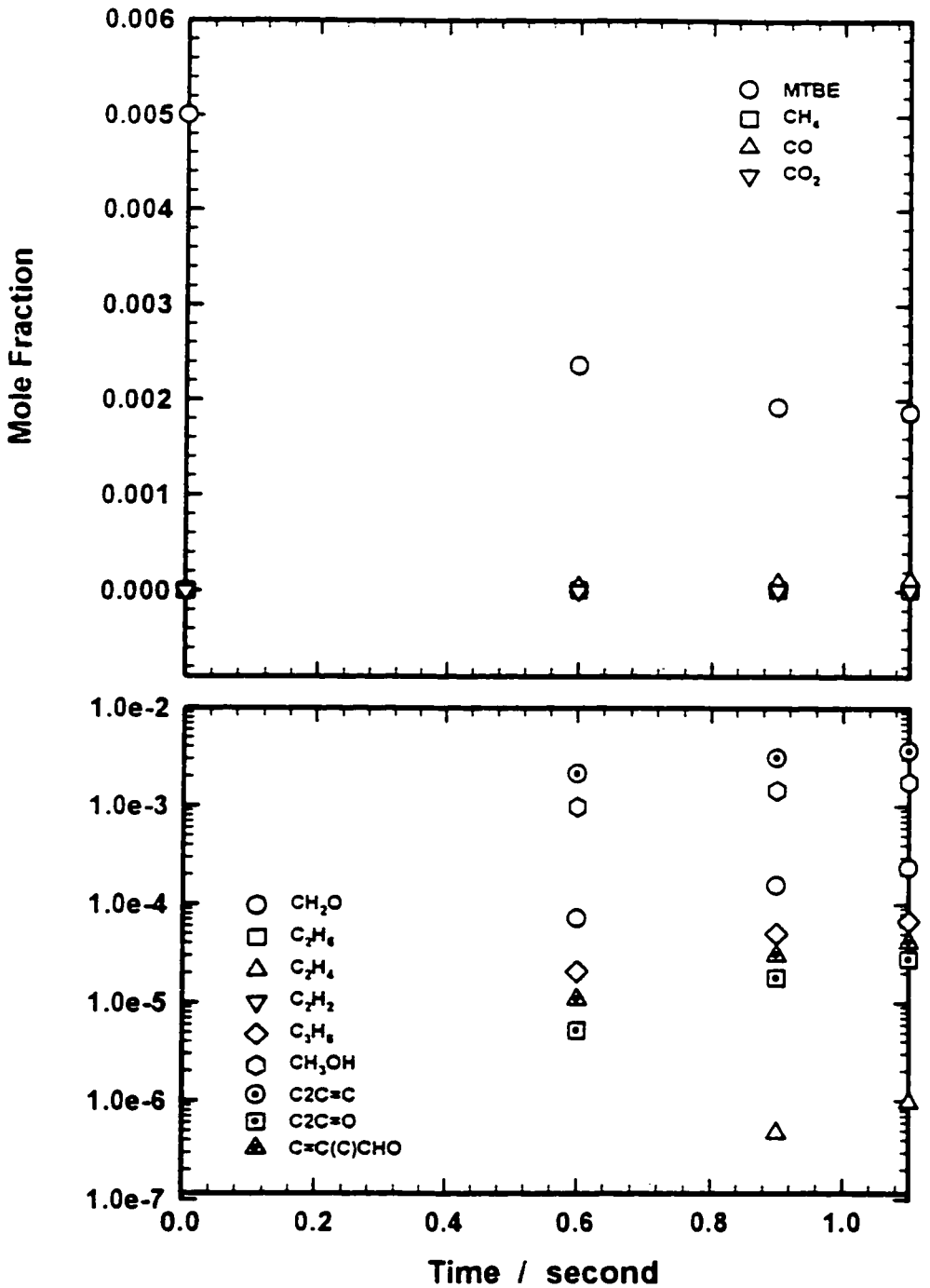


Figure IIC. 38 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 4 atm, T = 848 K

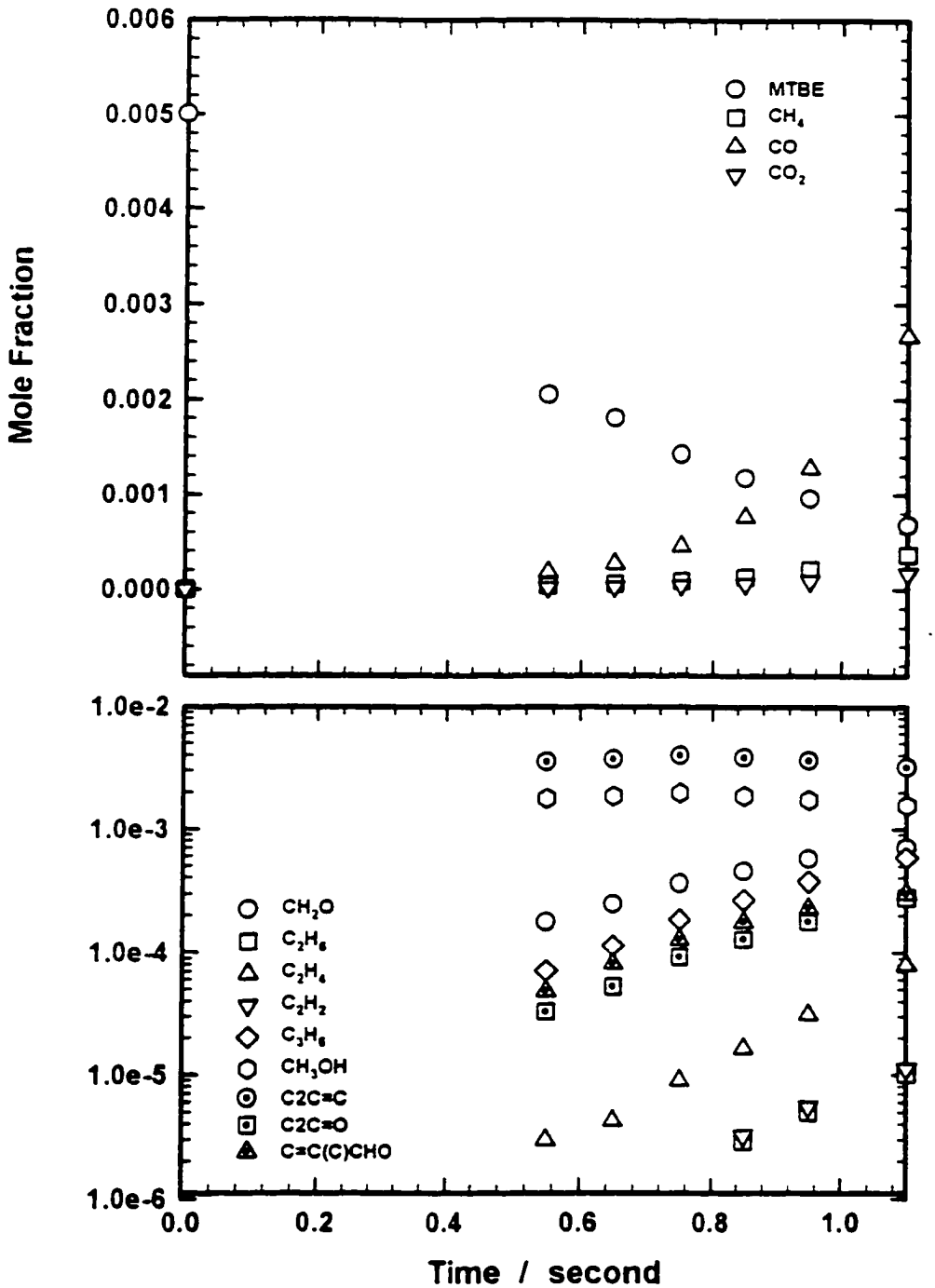


Figure IIC. 39 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 1.50$, P = 4 atm, T = 873 K

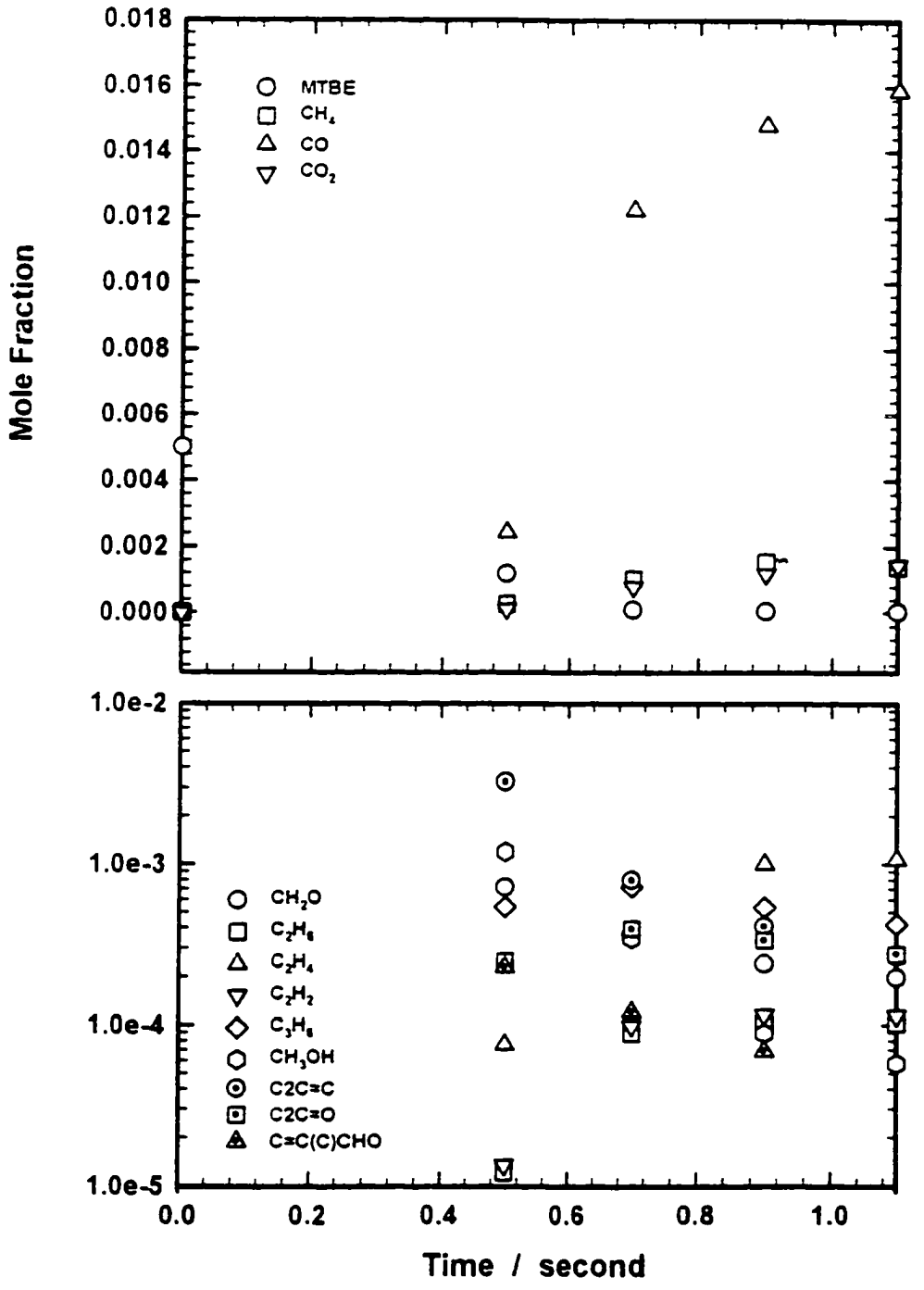


Figure IIC. 40 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 1.50$, P = 4 atm, T = 898 K

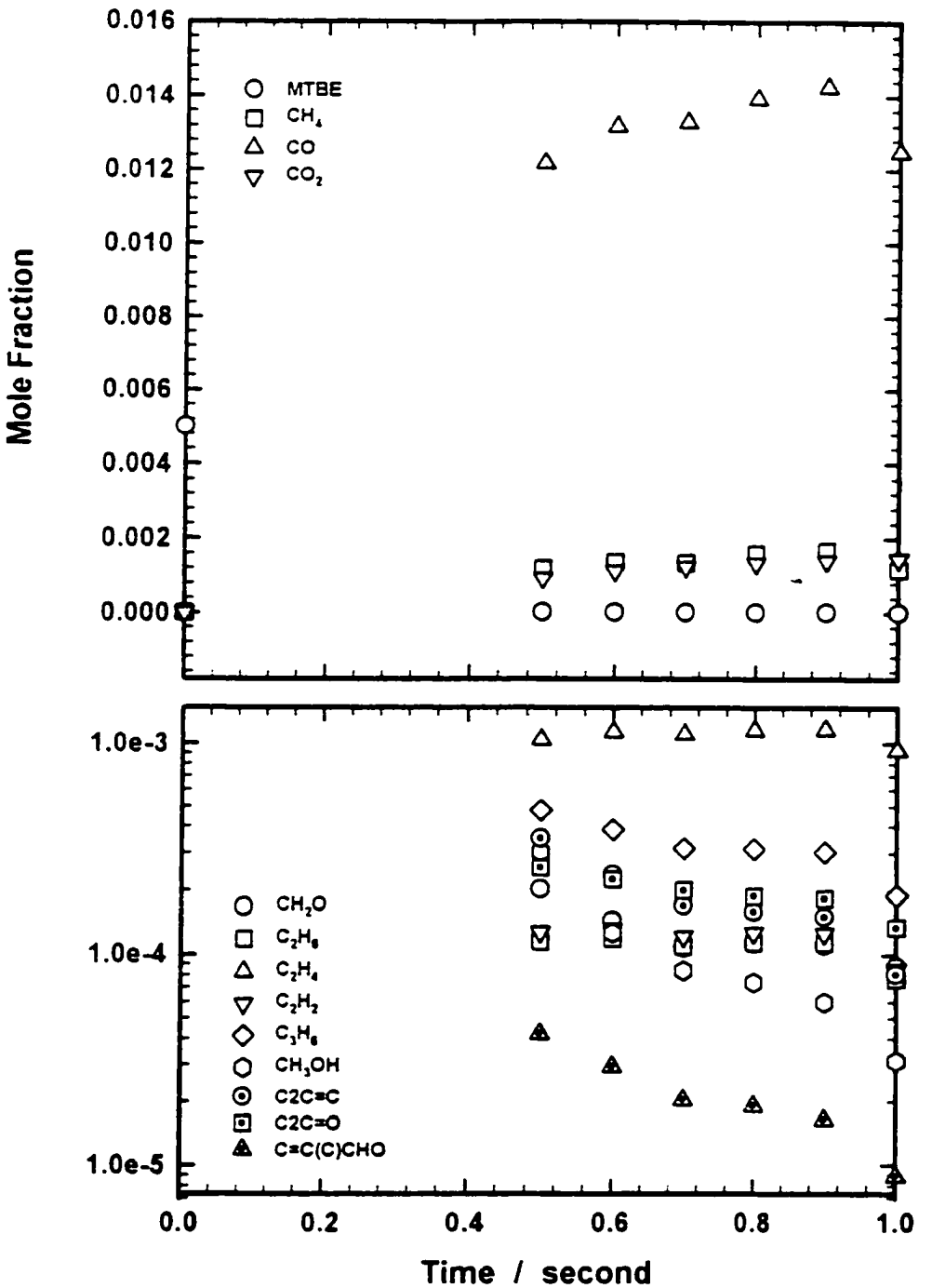


Figure IIC. 41 Experimental result of 0.5% MTBE oxidation product distribution at $\varphi = 1.50$, P = 4 atm, T = 923 K

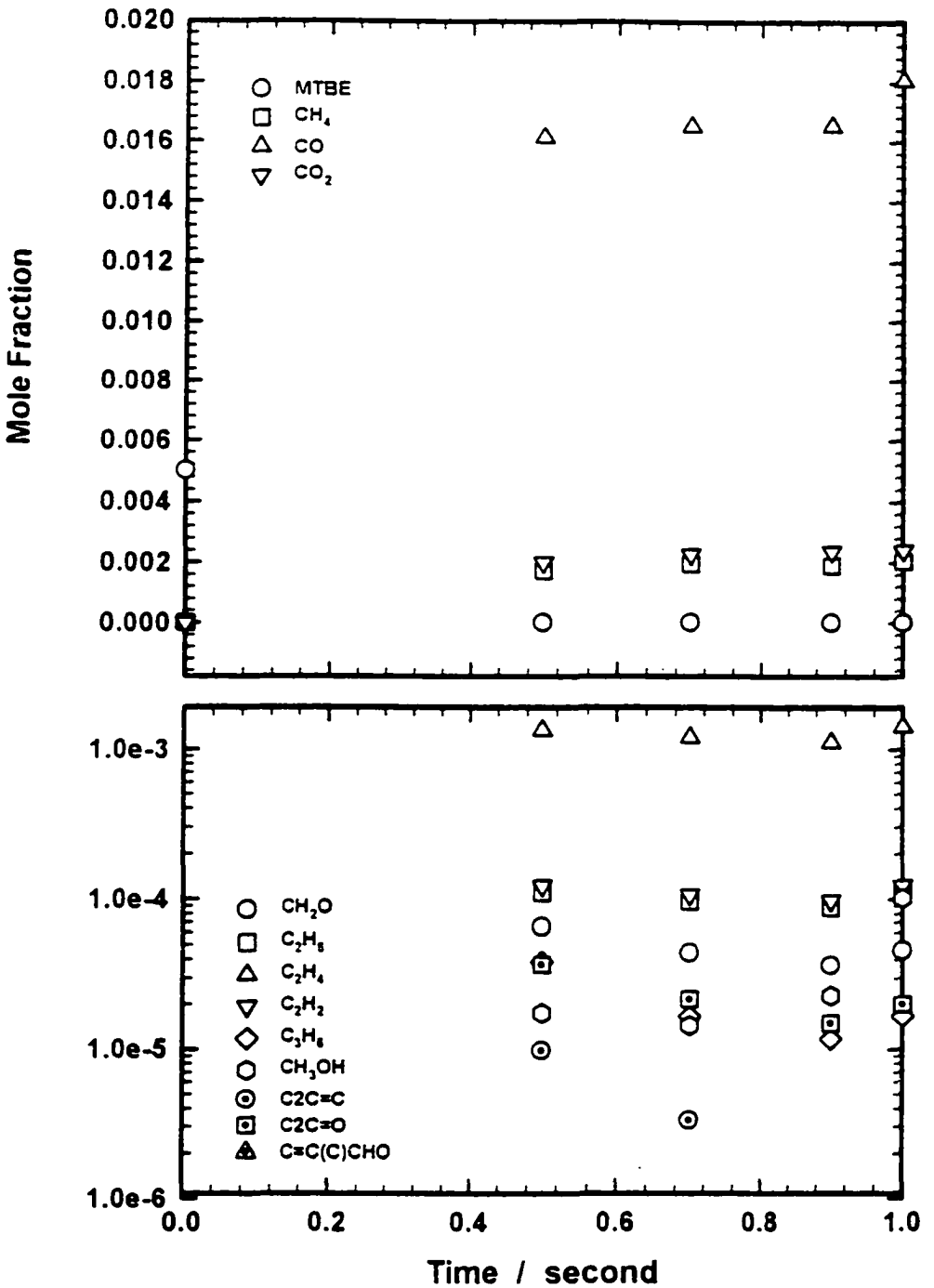


Figure IIC. 42 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 4 atm, T = 998 K

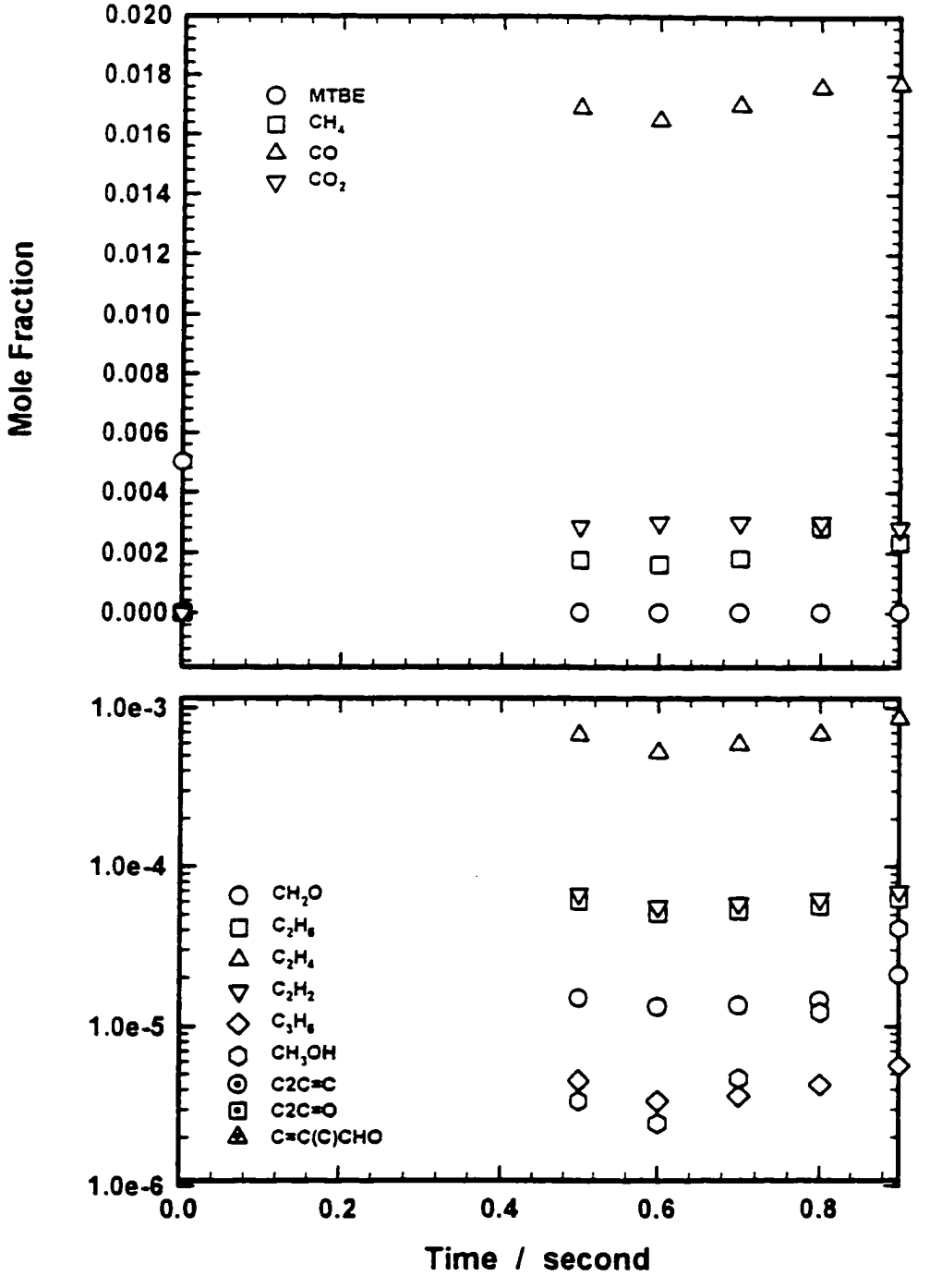


Figure IIC. 43 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 4 atm, T = 1048 K

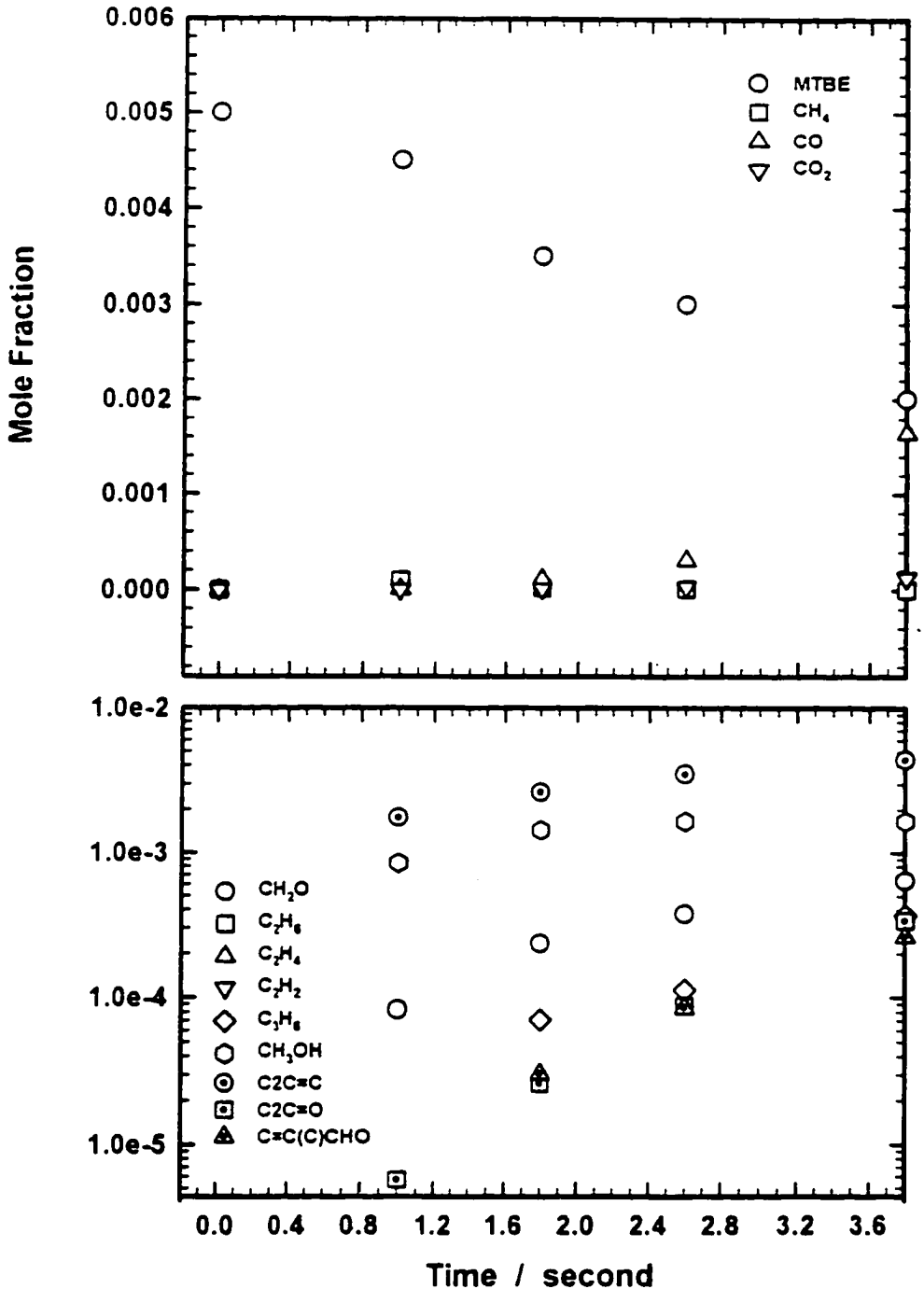


Figure IIC. 44 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 7 atm, T = 798 K

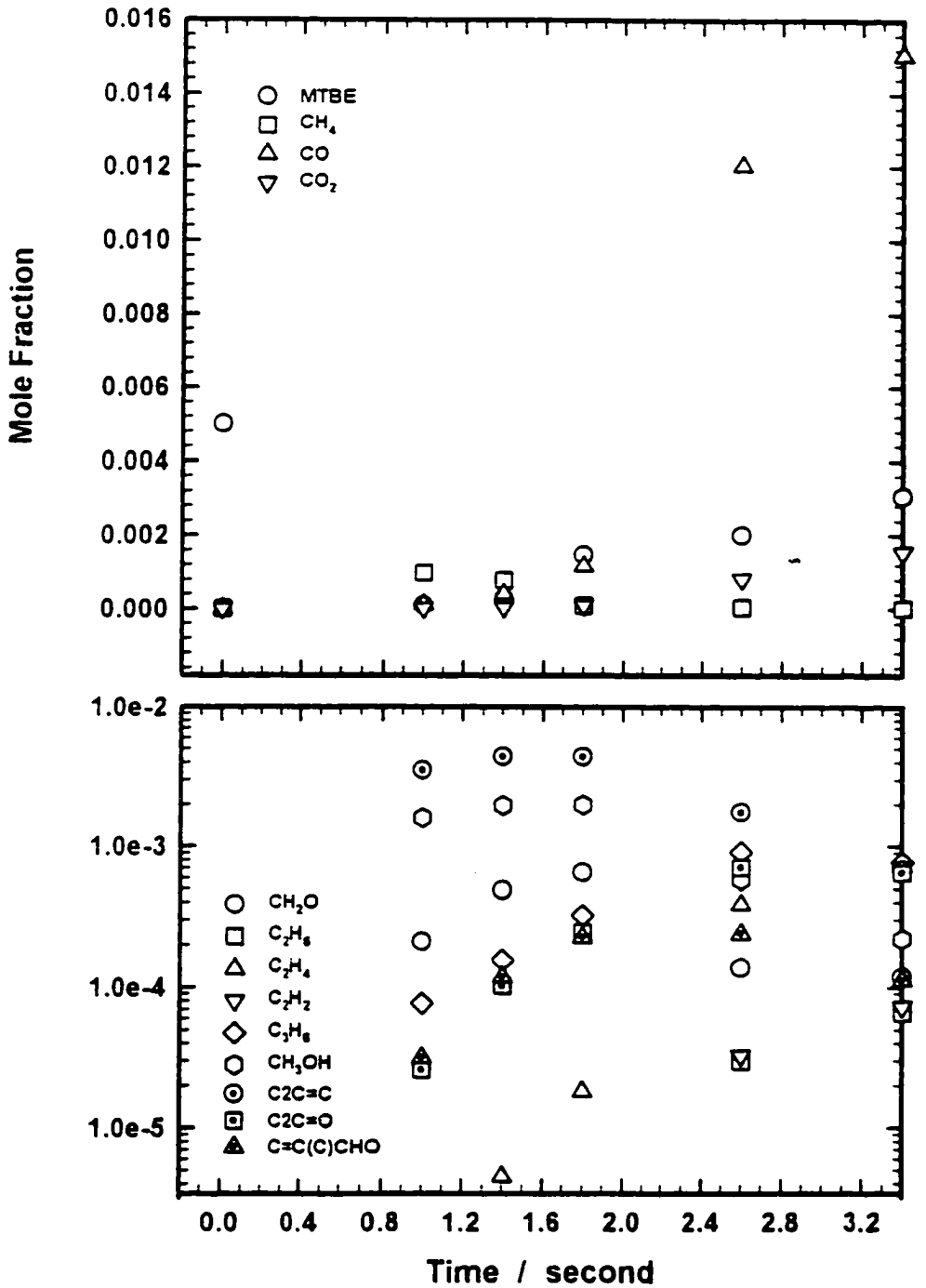


Figure IIC. 45 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 7 atm, T = 823 K

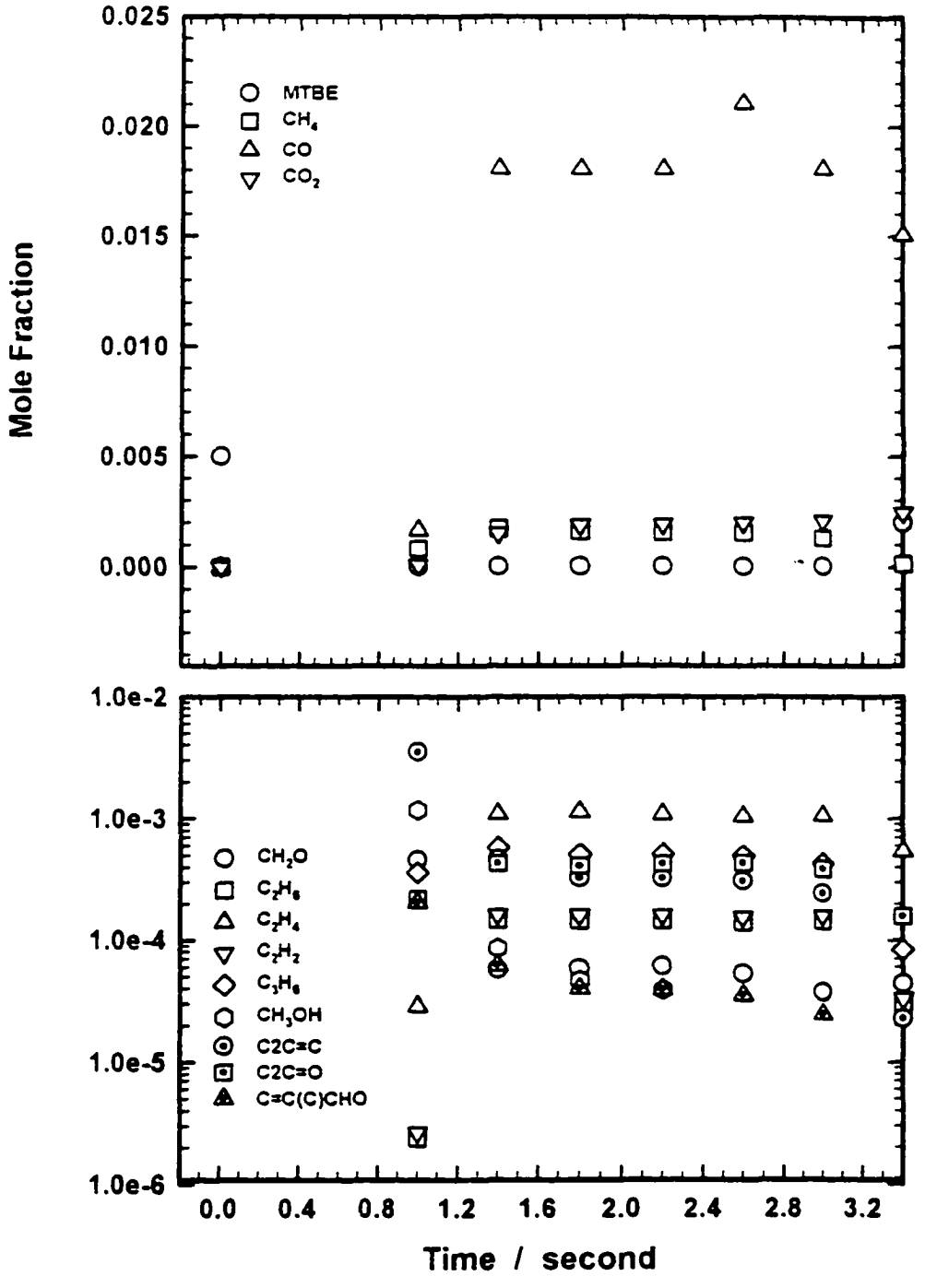


Figure IIC. 46 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 7 atm, T = 848 K

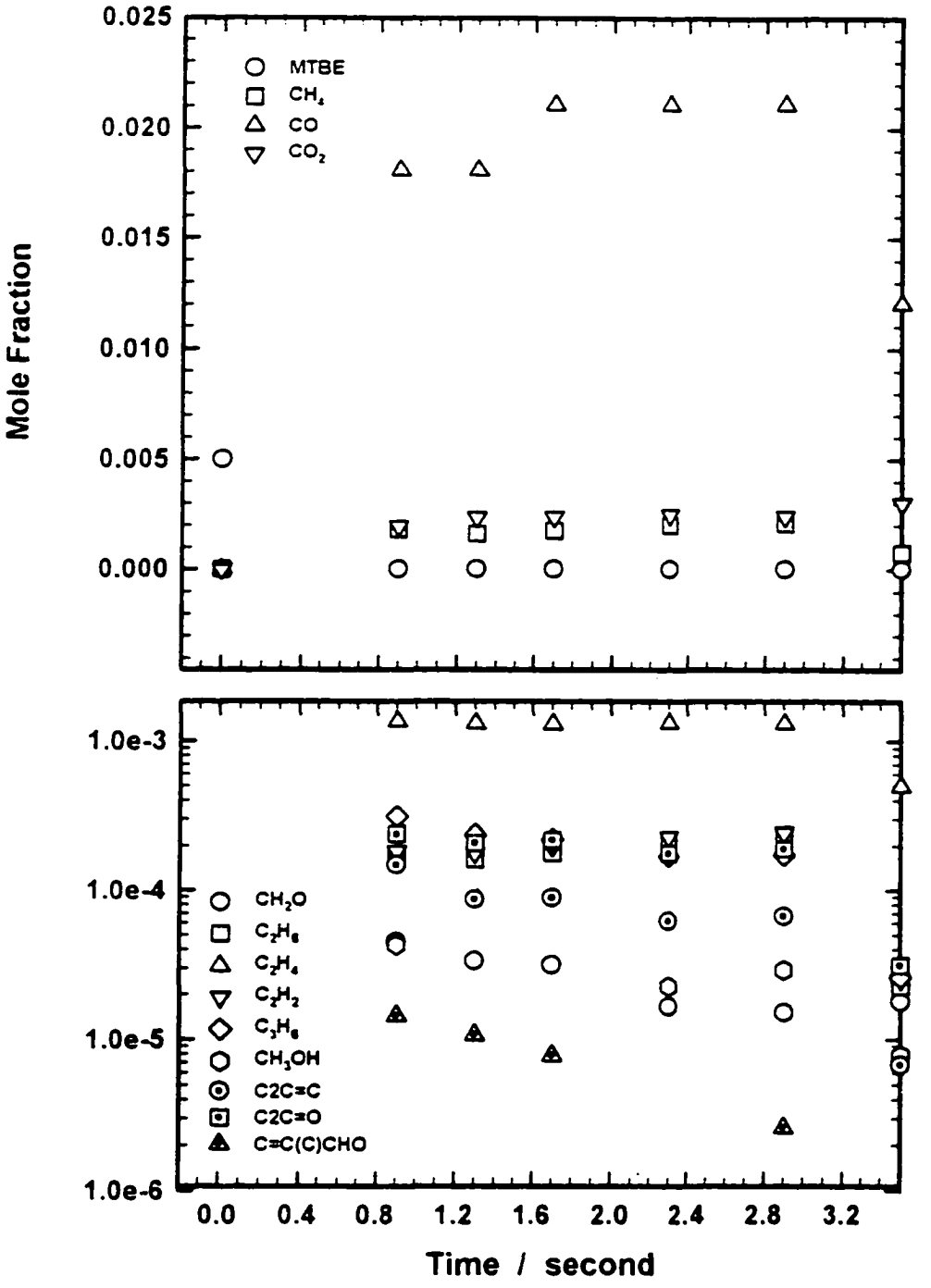


Figure IIC. 47 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 7 atm, T = 873 K

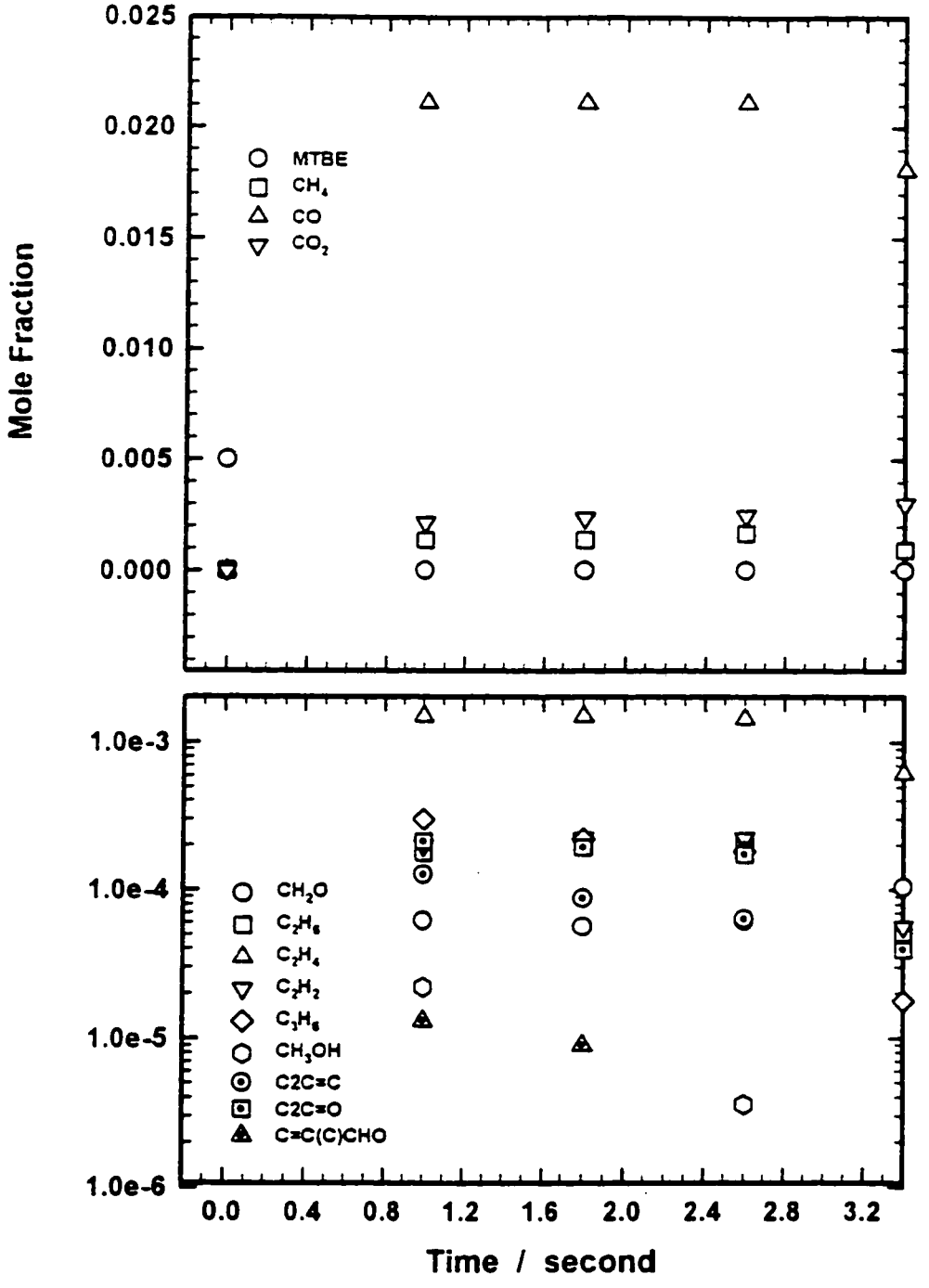


Figure IIC. 48 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 7 atm, T = 898 K

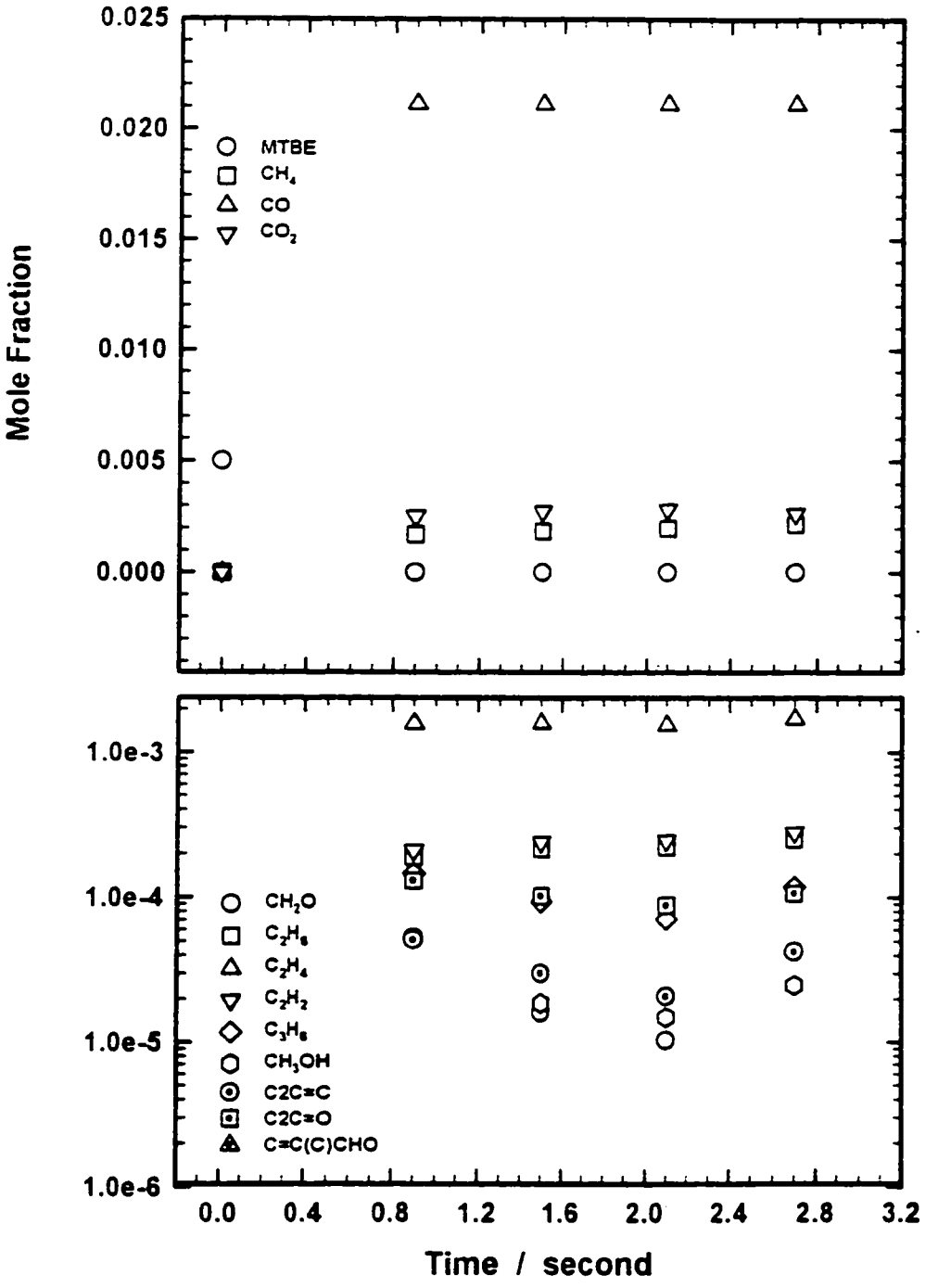


Figure IIC. 49 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 7 atm, T = 923 K

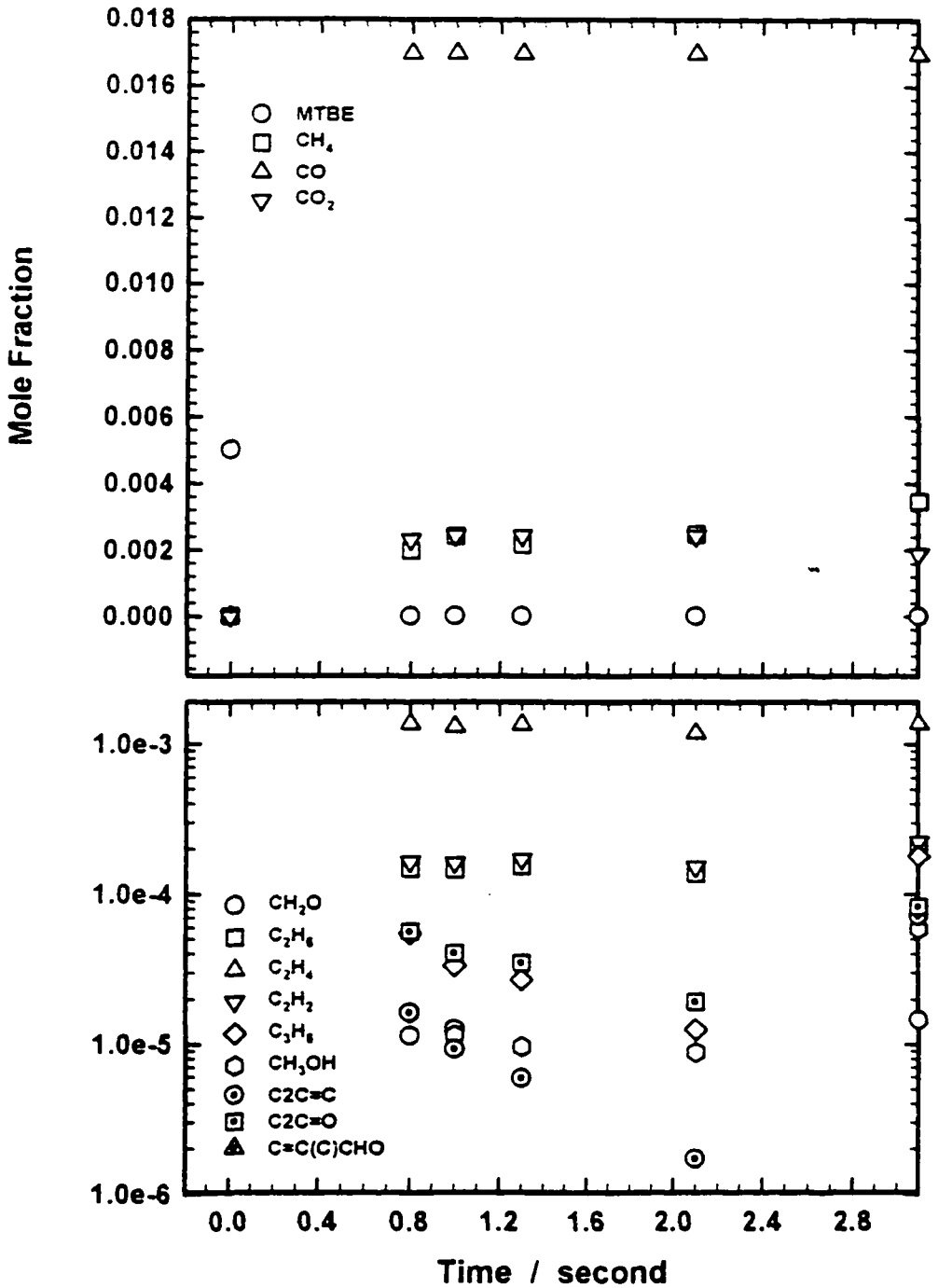


Figure IIC. 50 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 7 atm, T = 973 K

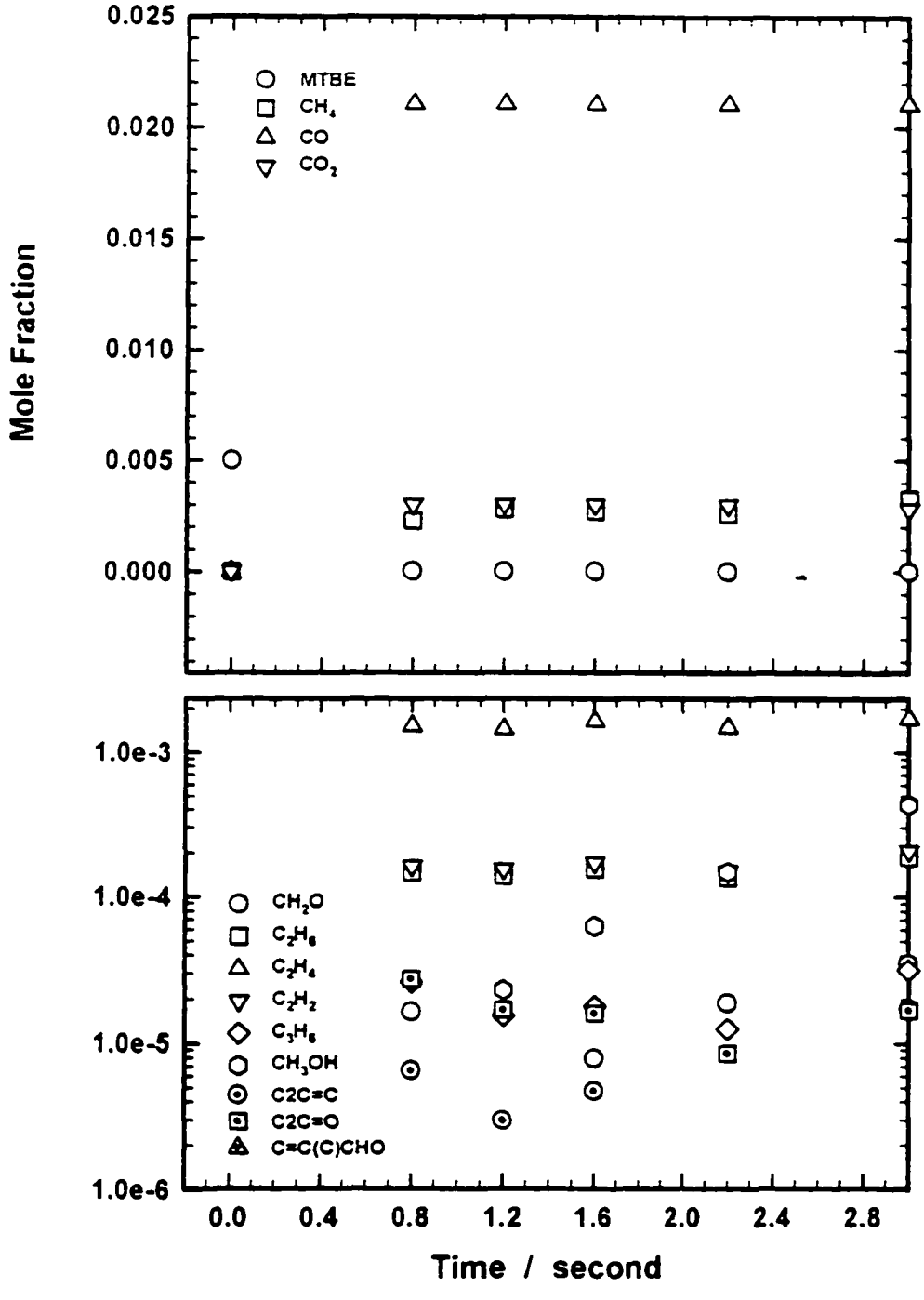


Figure IIC. 51 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 7 atm, T = 998 K

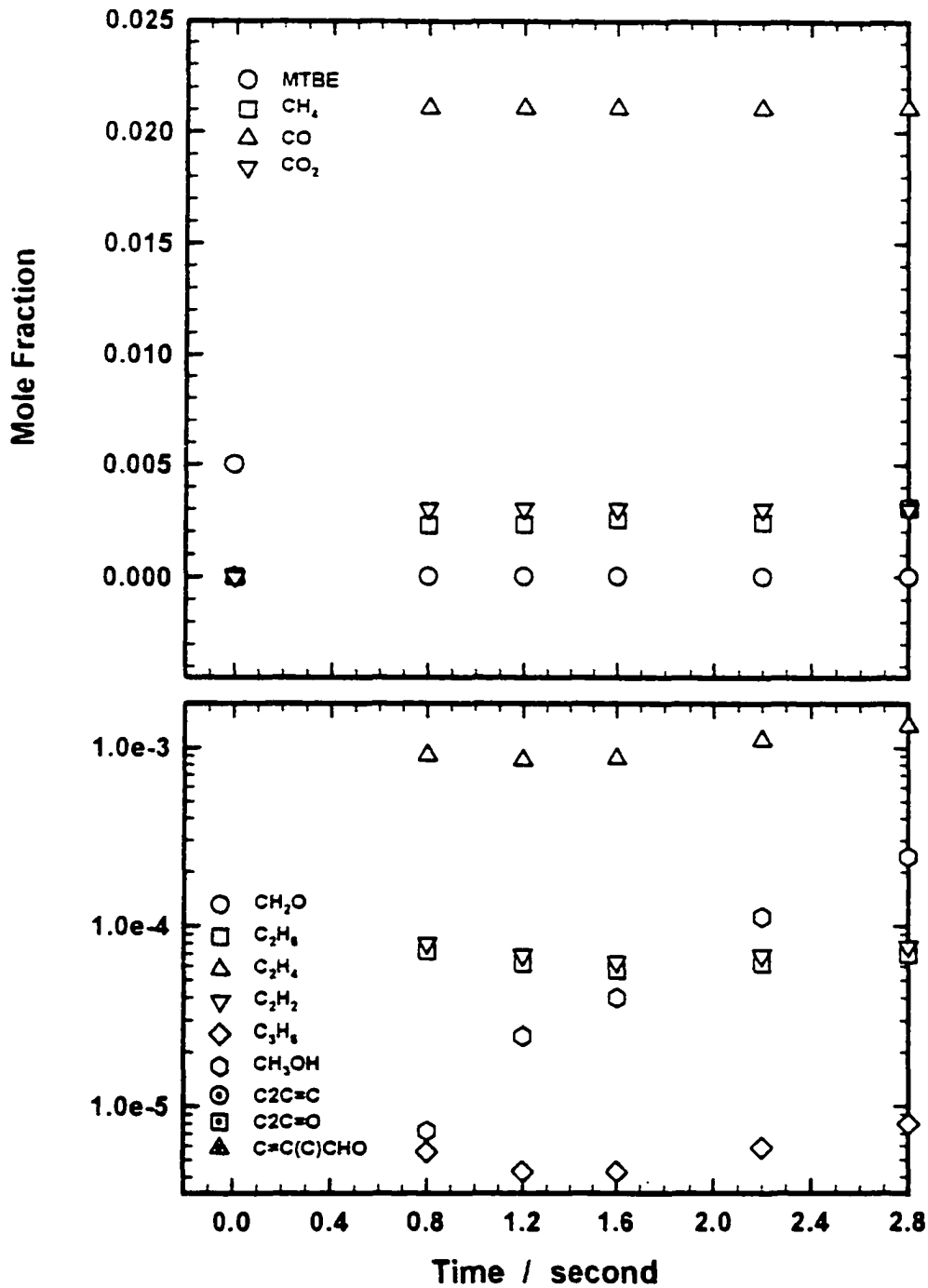


Figure IIC. 52 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 7 atm, T = 1048 K

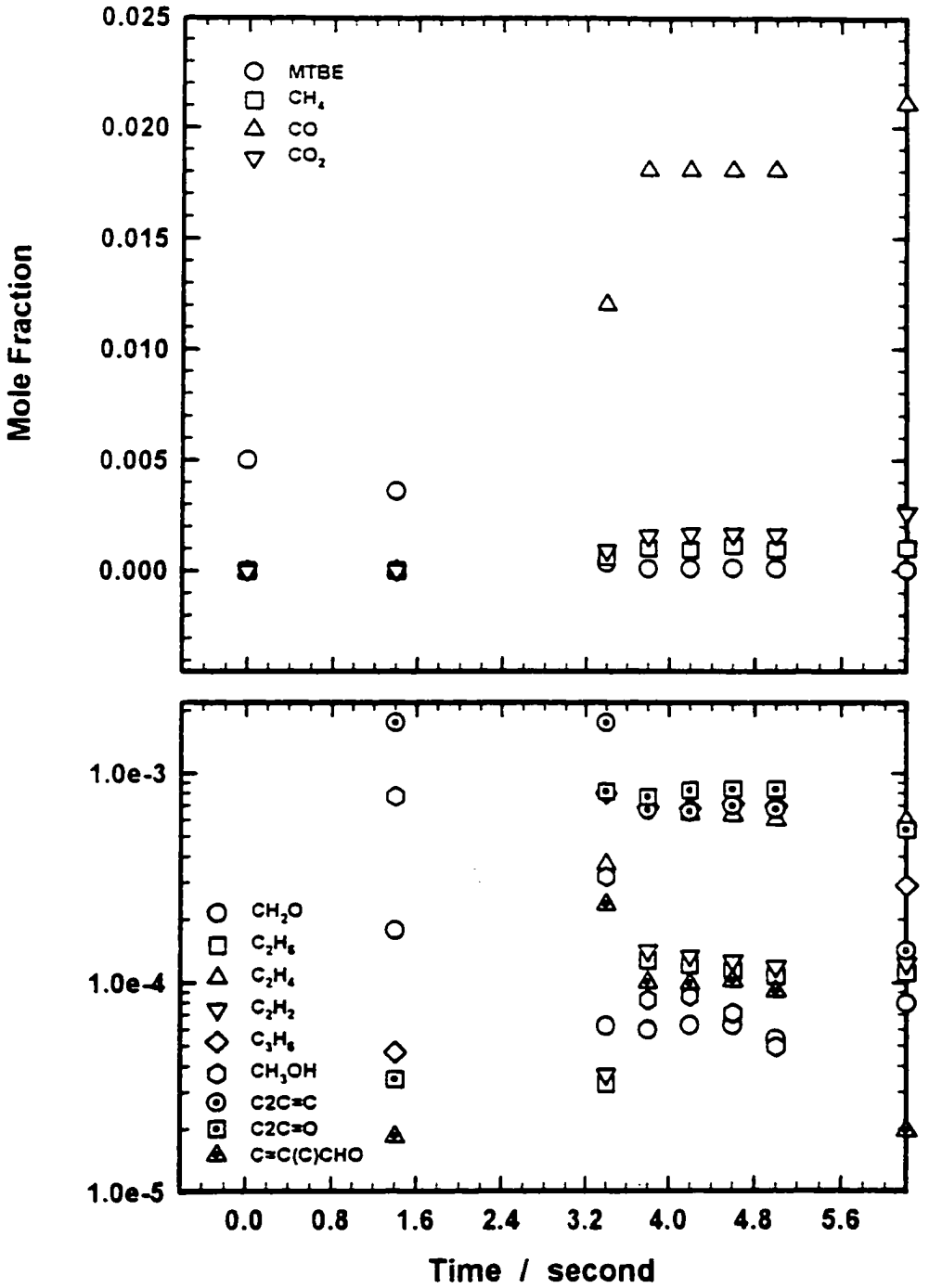


Figure IIC. 53 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 10 atm, T = 798 K

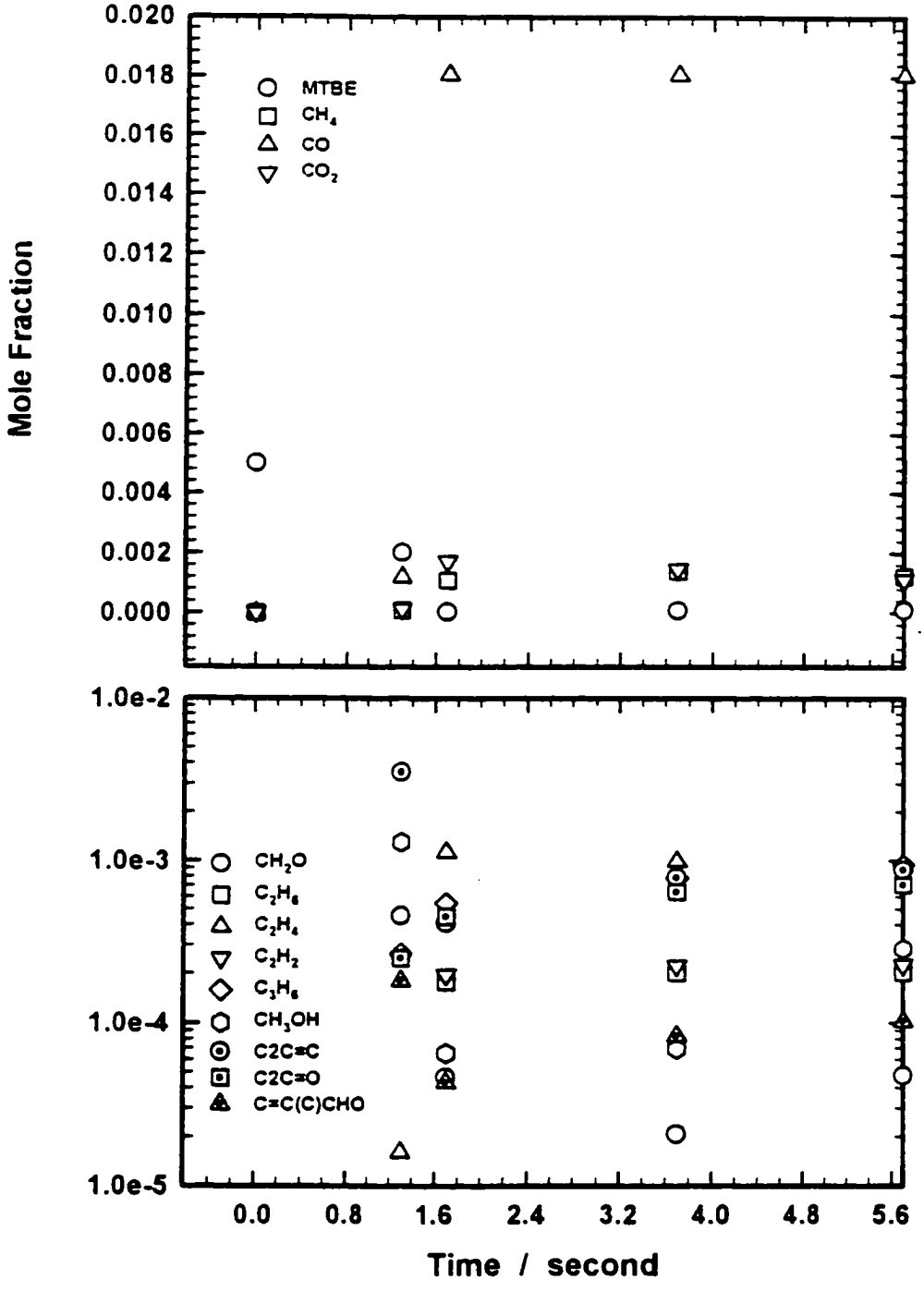


Figure IIC. 54 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 10 atm, T = 823 K

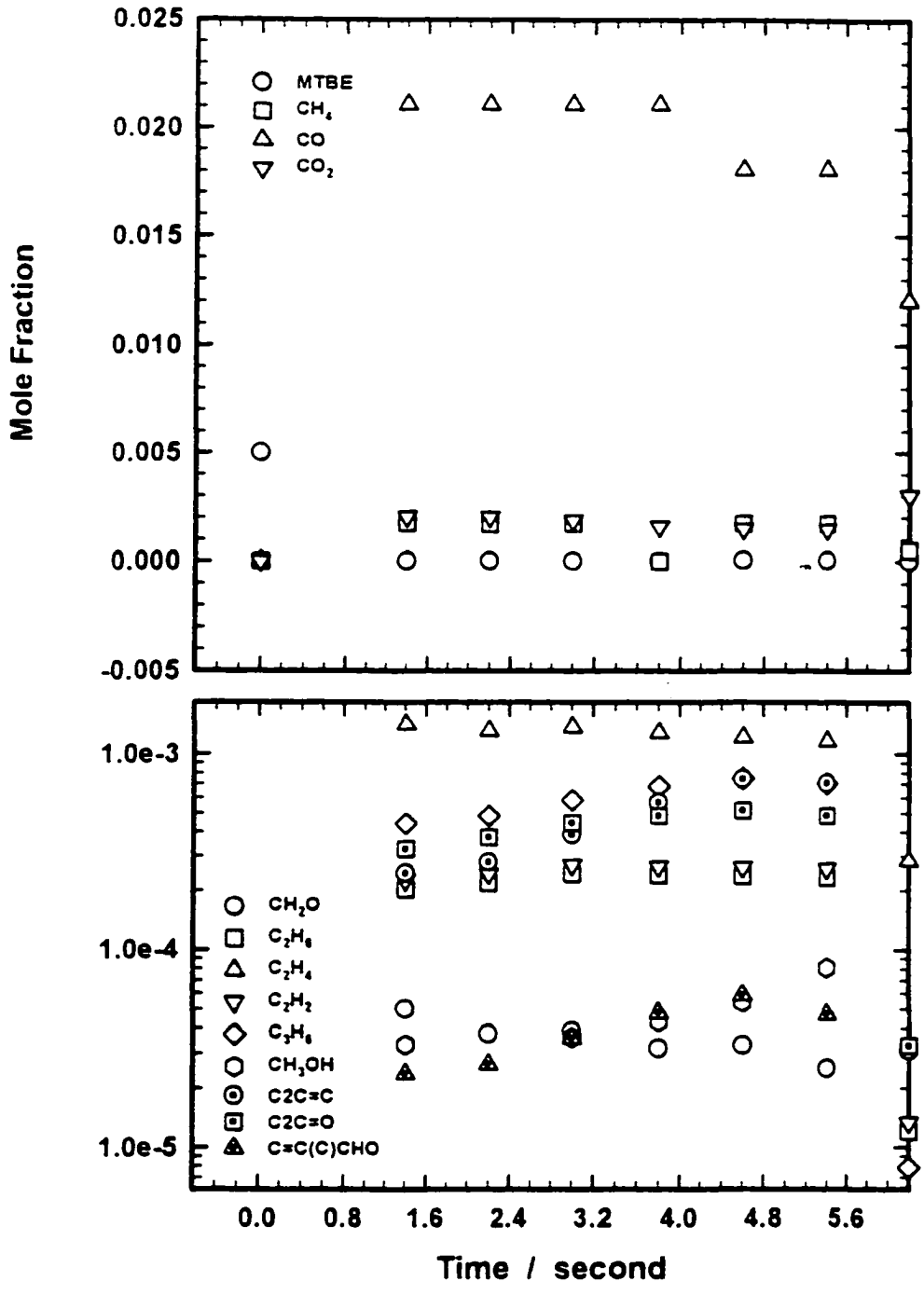


Figure IIC. 55 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 10 atm, T = 848 K

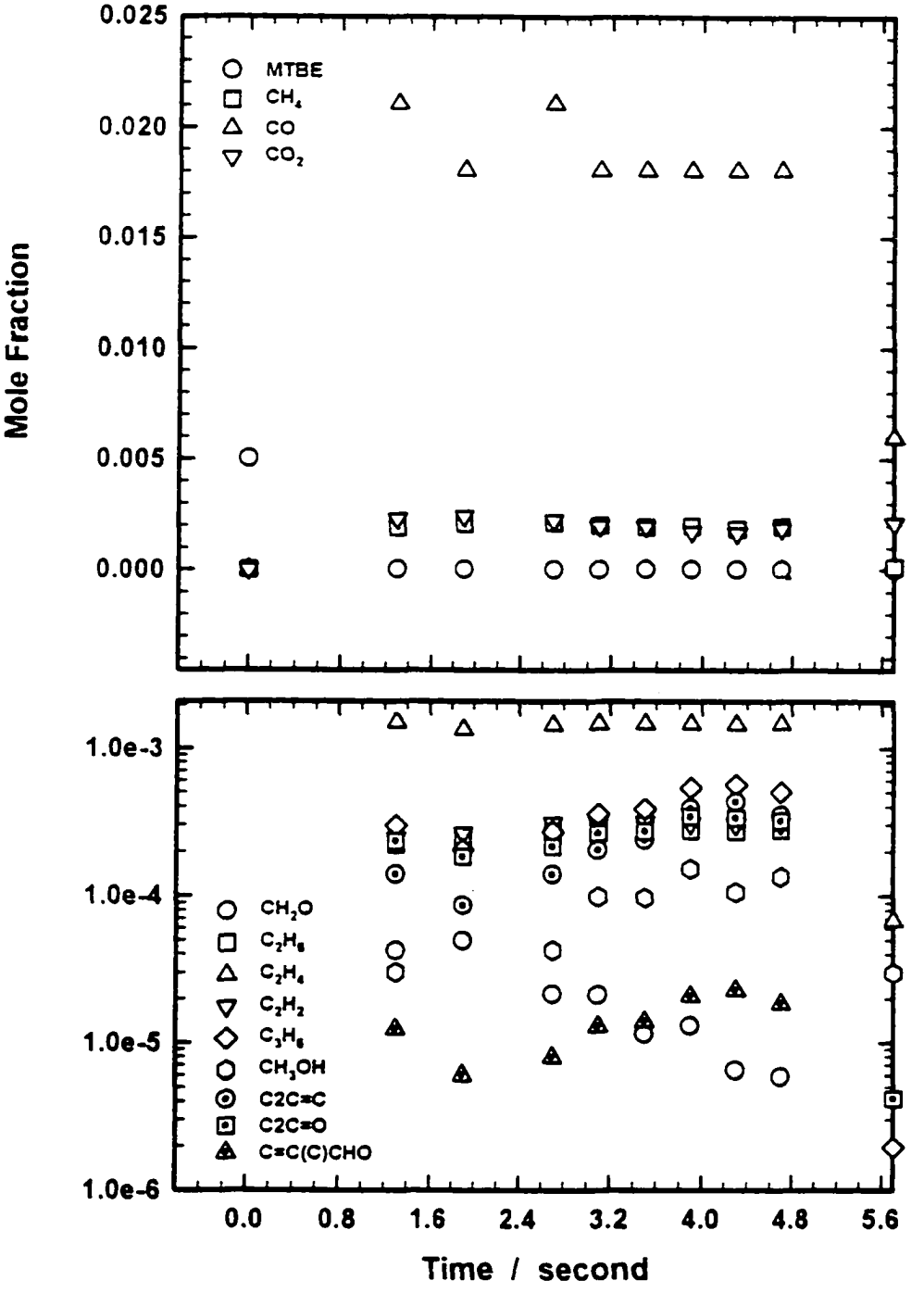


Figure IIC. 56 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 10 atm, T = 873 K

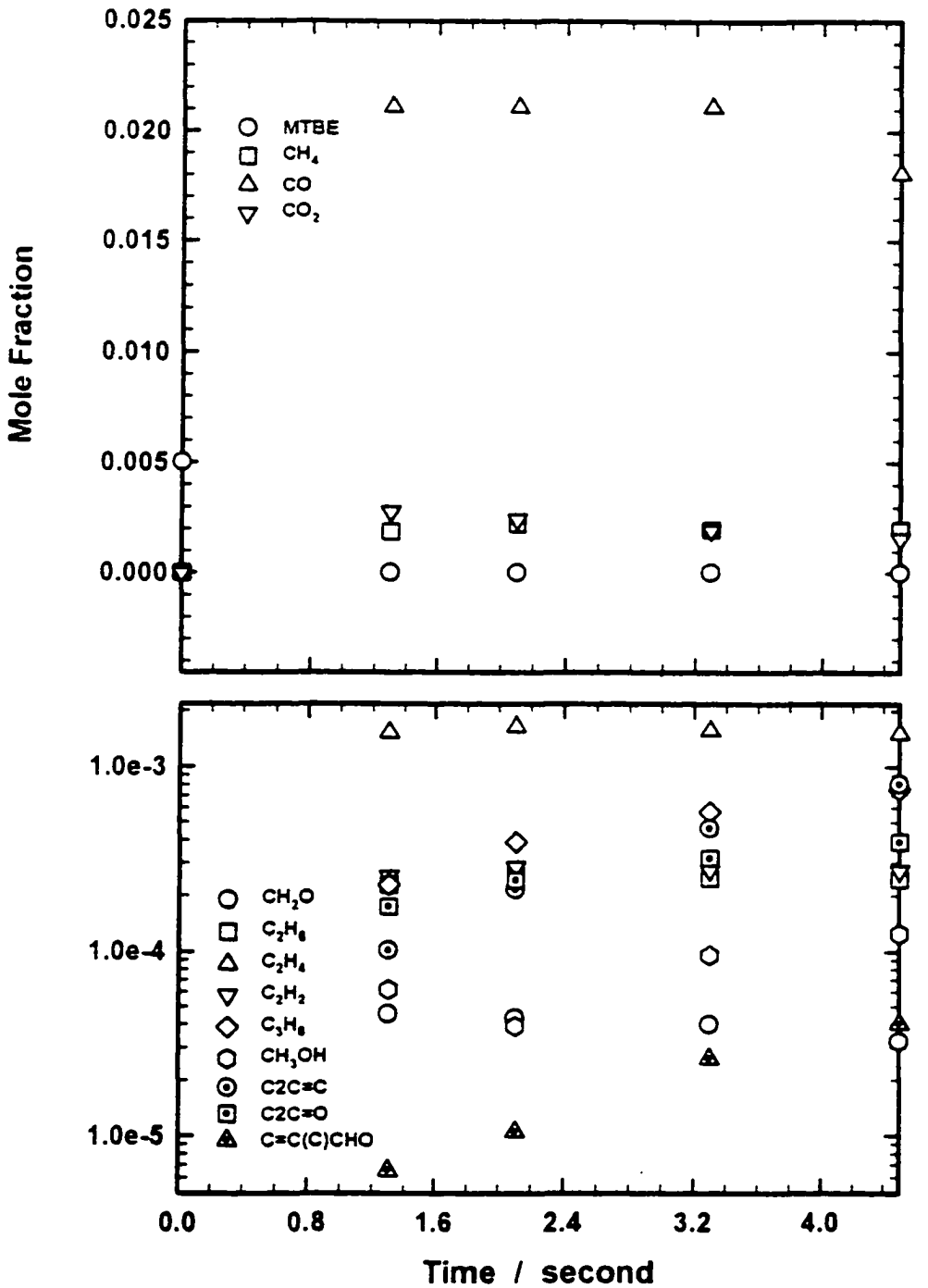


Figure IIC. 57 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 10 atm, T = 898 K

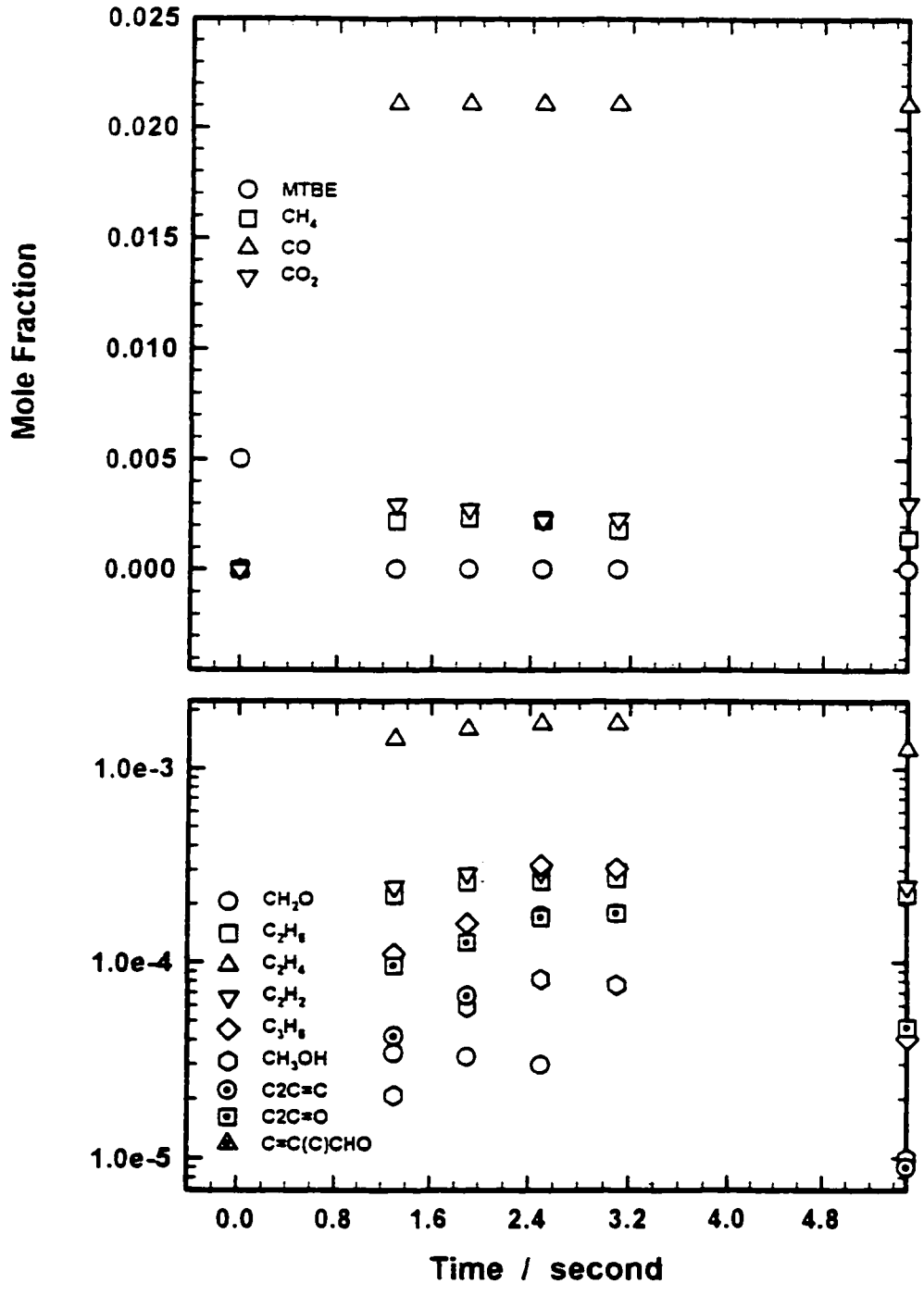


Figure IIC. 58 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 10 atm, T = 923 K

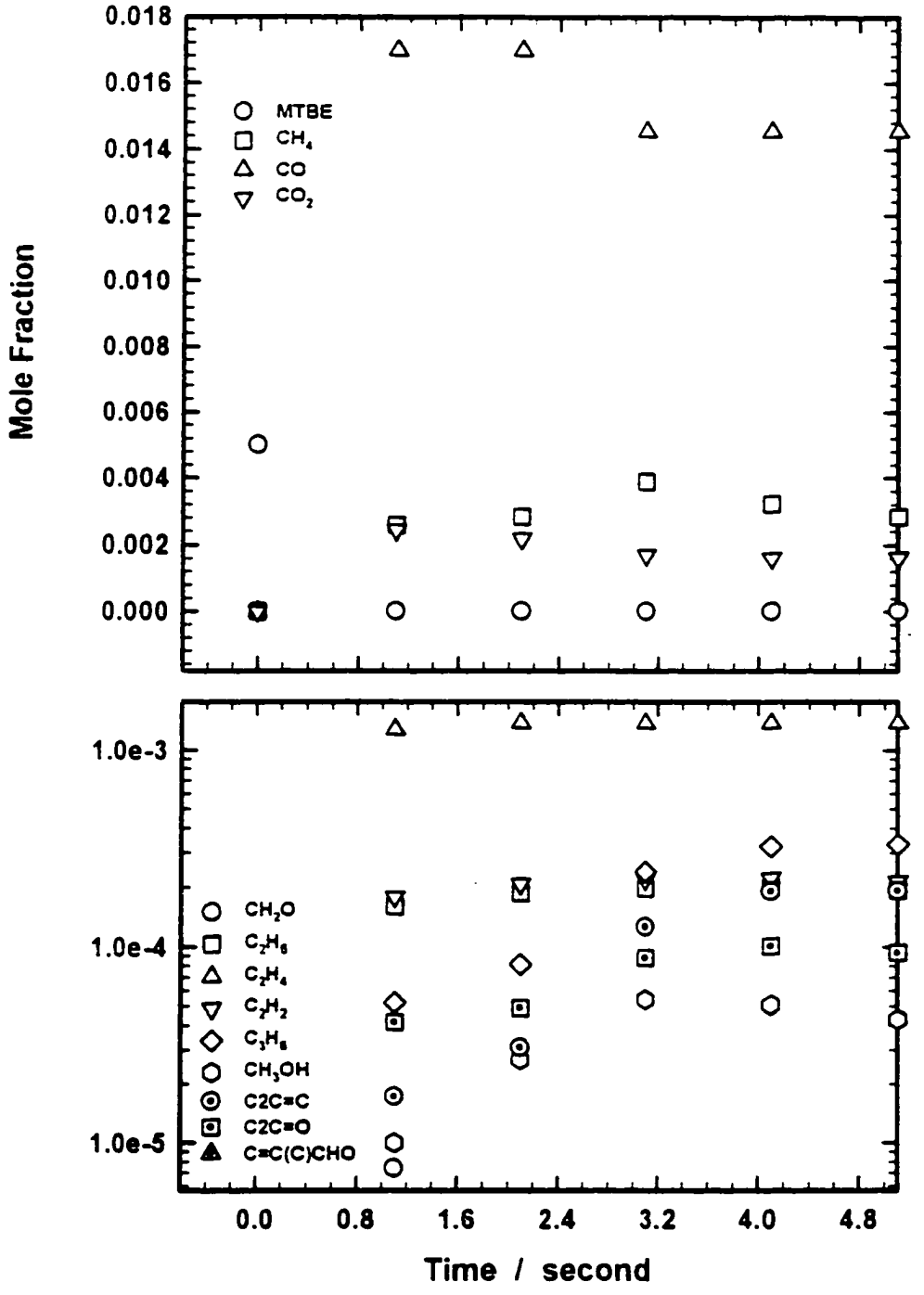


Figure IIC. 59 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 10 atm, T = 973 K

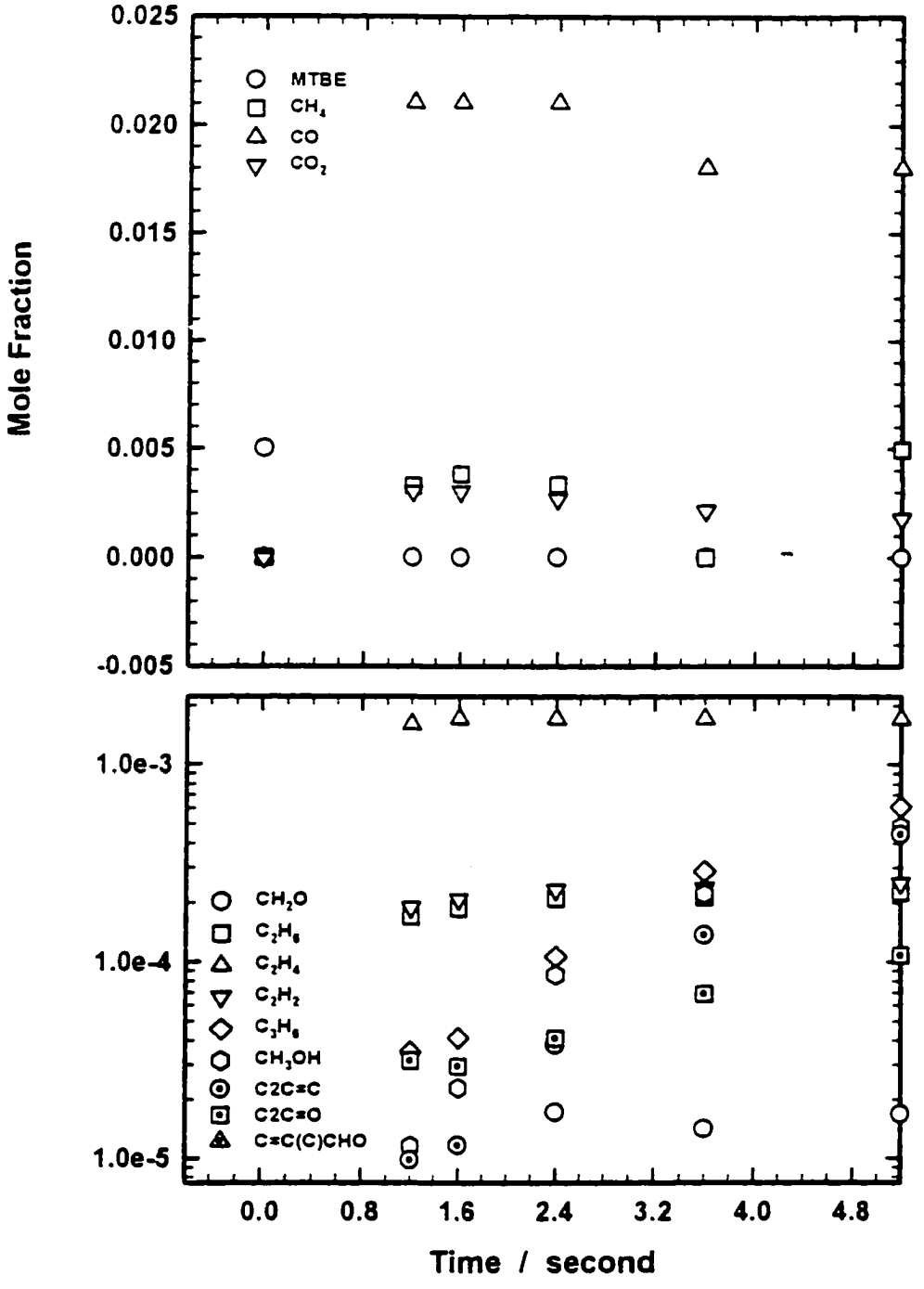


Figure IIC. 60 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 10 atm, T = 998 K

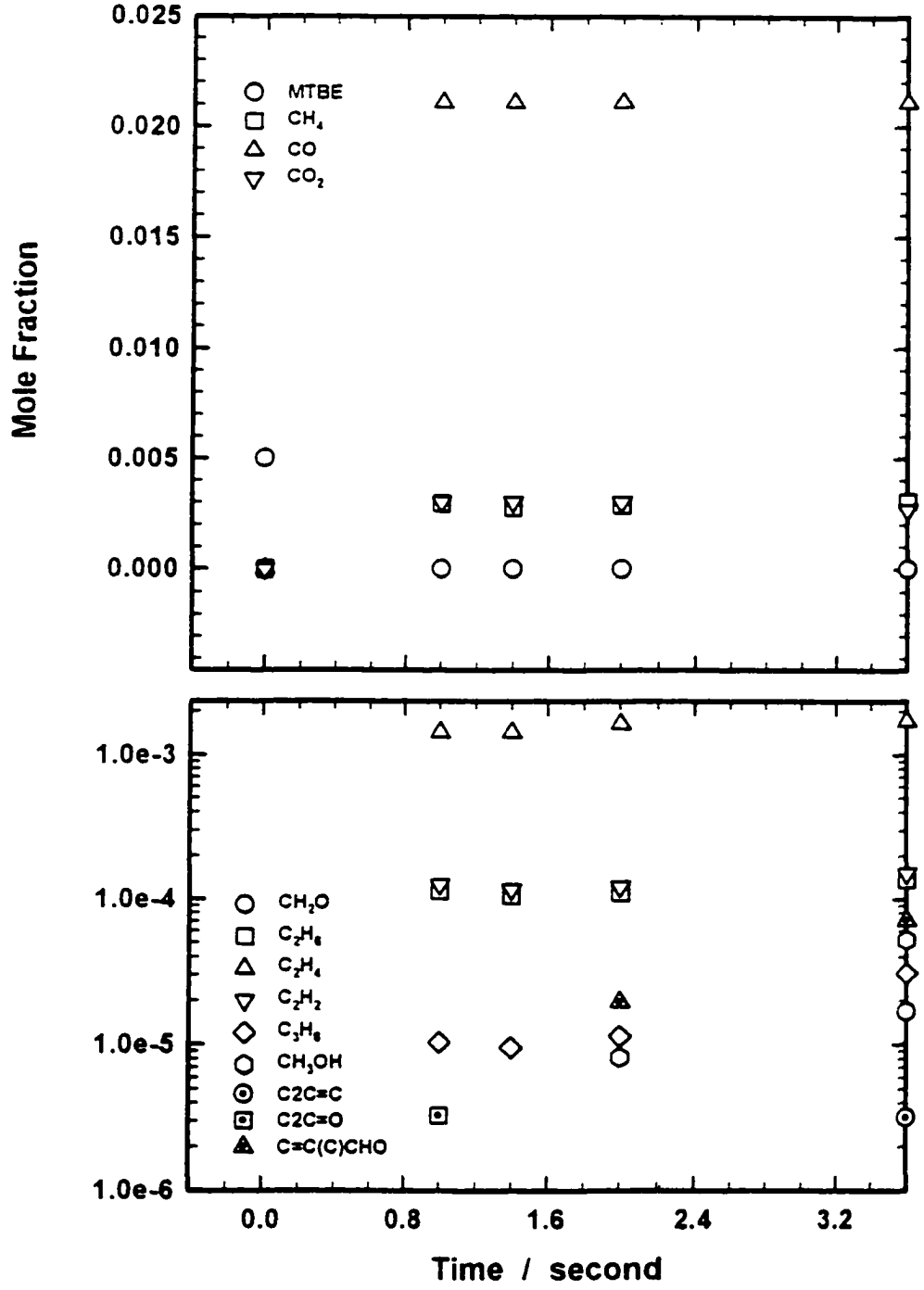


Figure IIC. 61 Experimental result of 0.5% MTBE oxidation product distribution at φ = 1.50, P = 10 atm, T = 1048 K

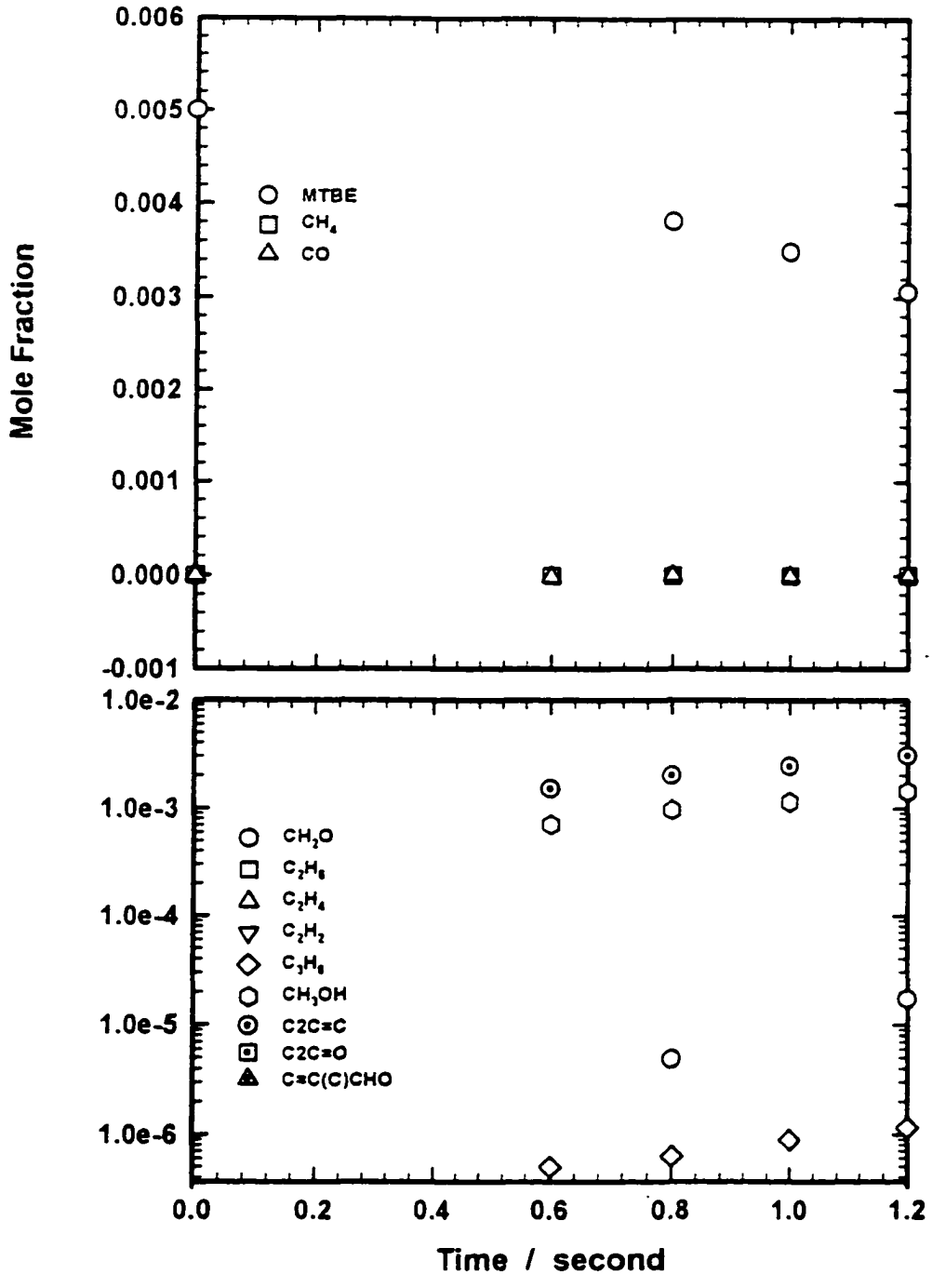


Figure IIC. 62 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 4 atm, T = 823 K

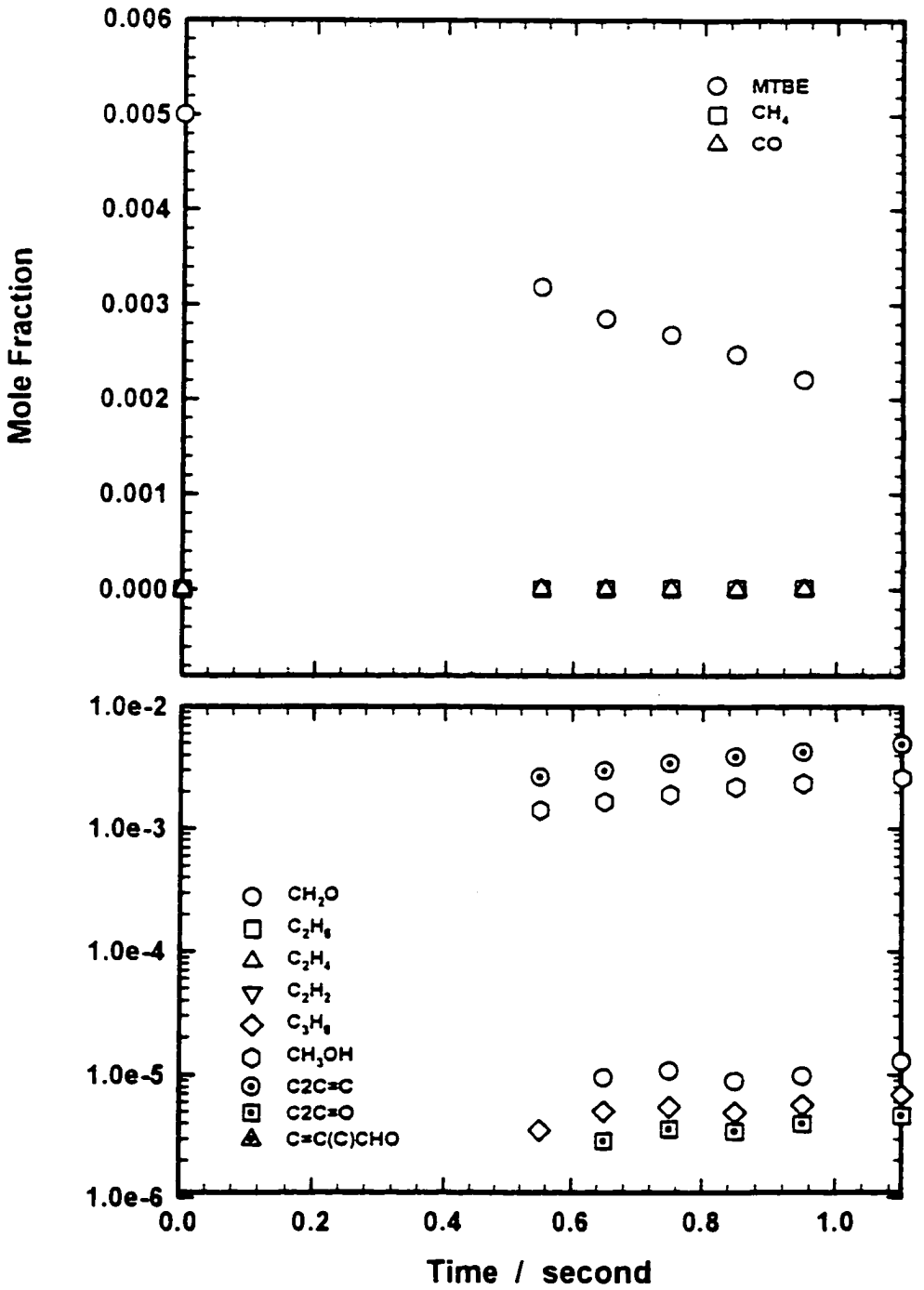


Figure IIC. 63 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 4 atm, T = 873 K

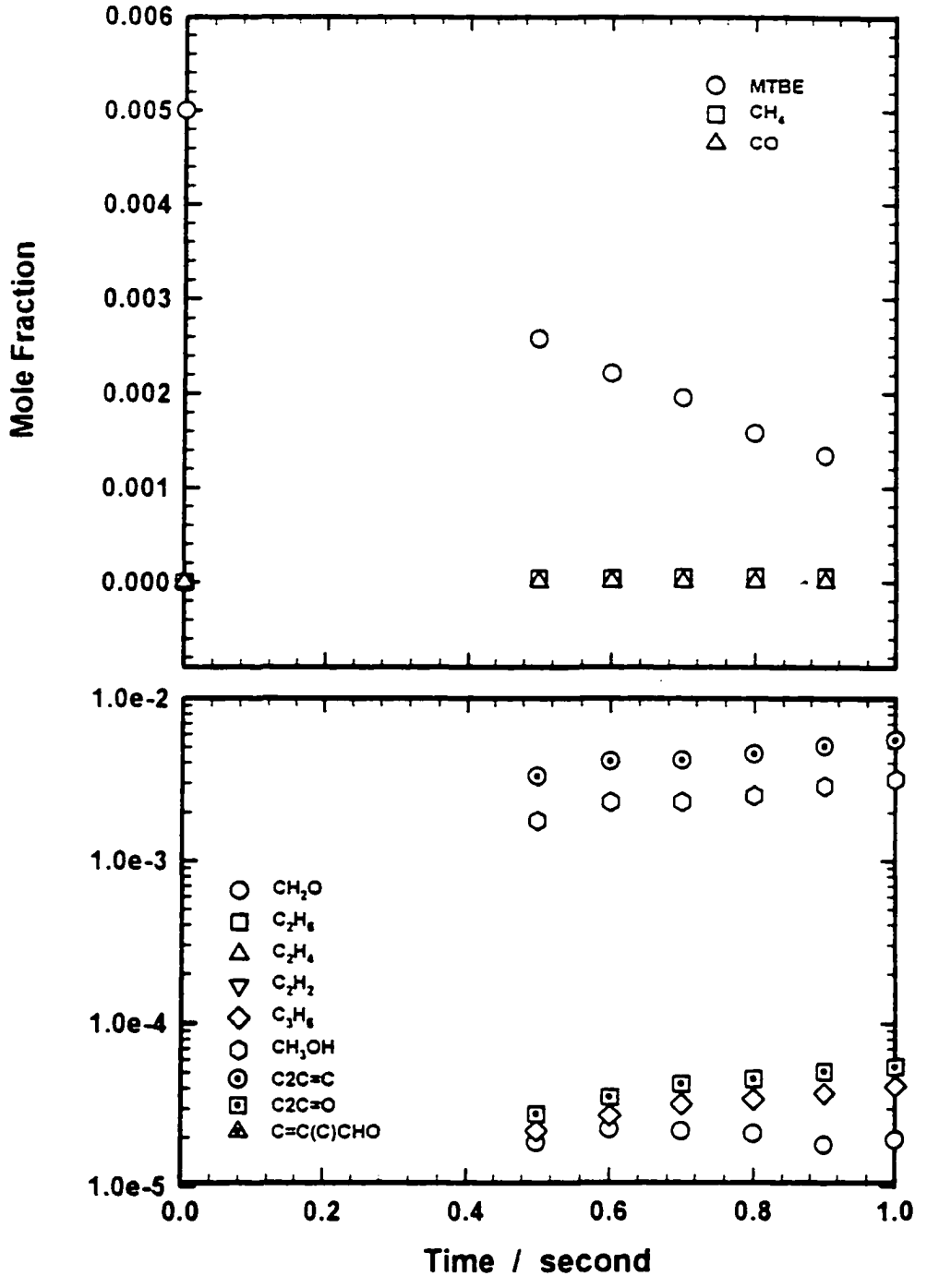


Figure IIC. 64 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 4 atm, T = 923 K

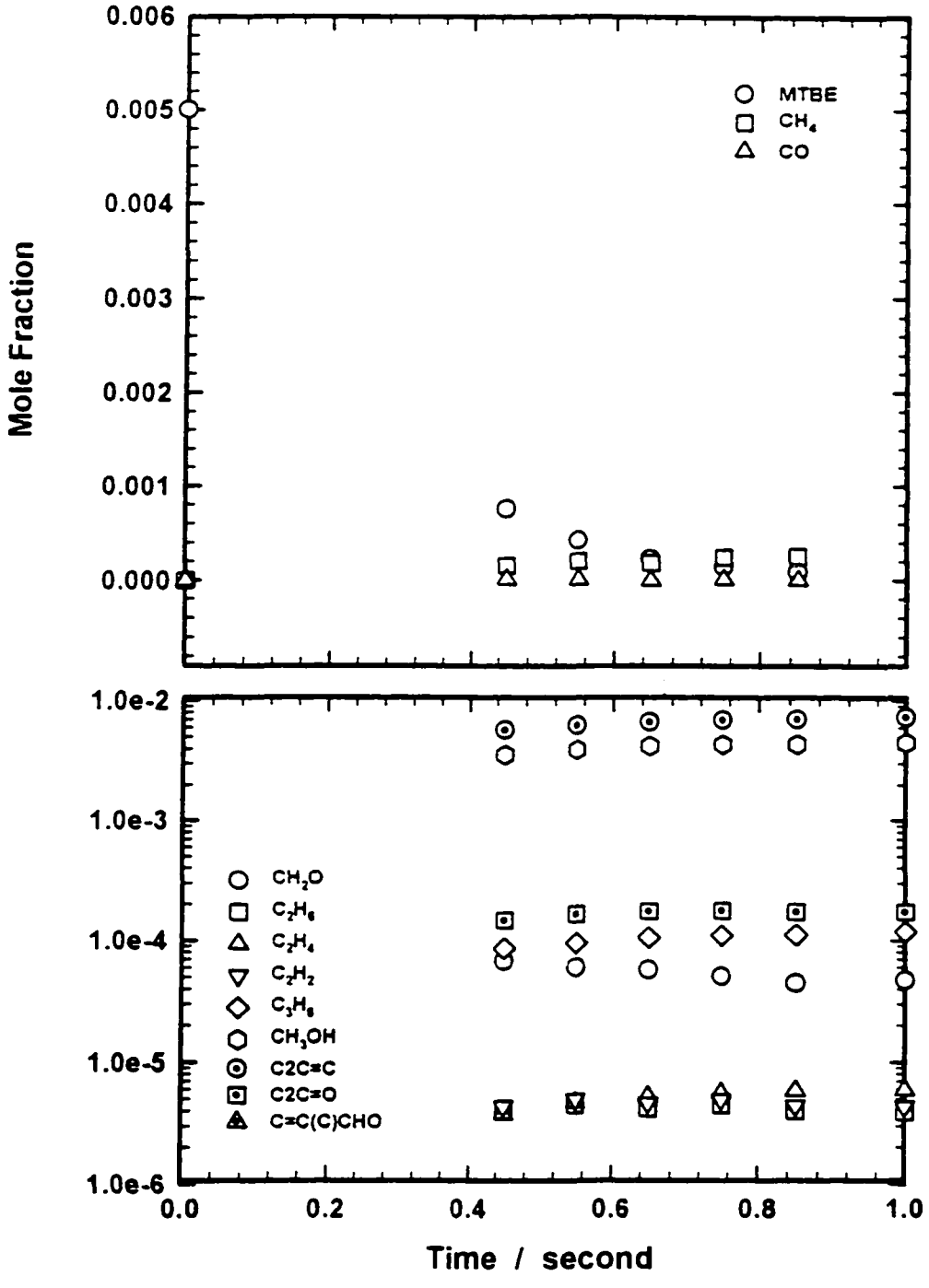


Figure IIC. 65 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 4 atm, T = 973 K

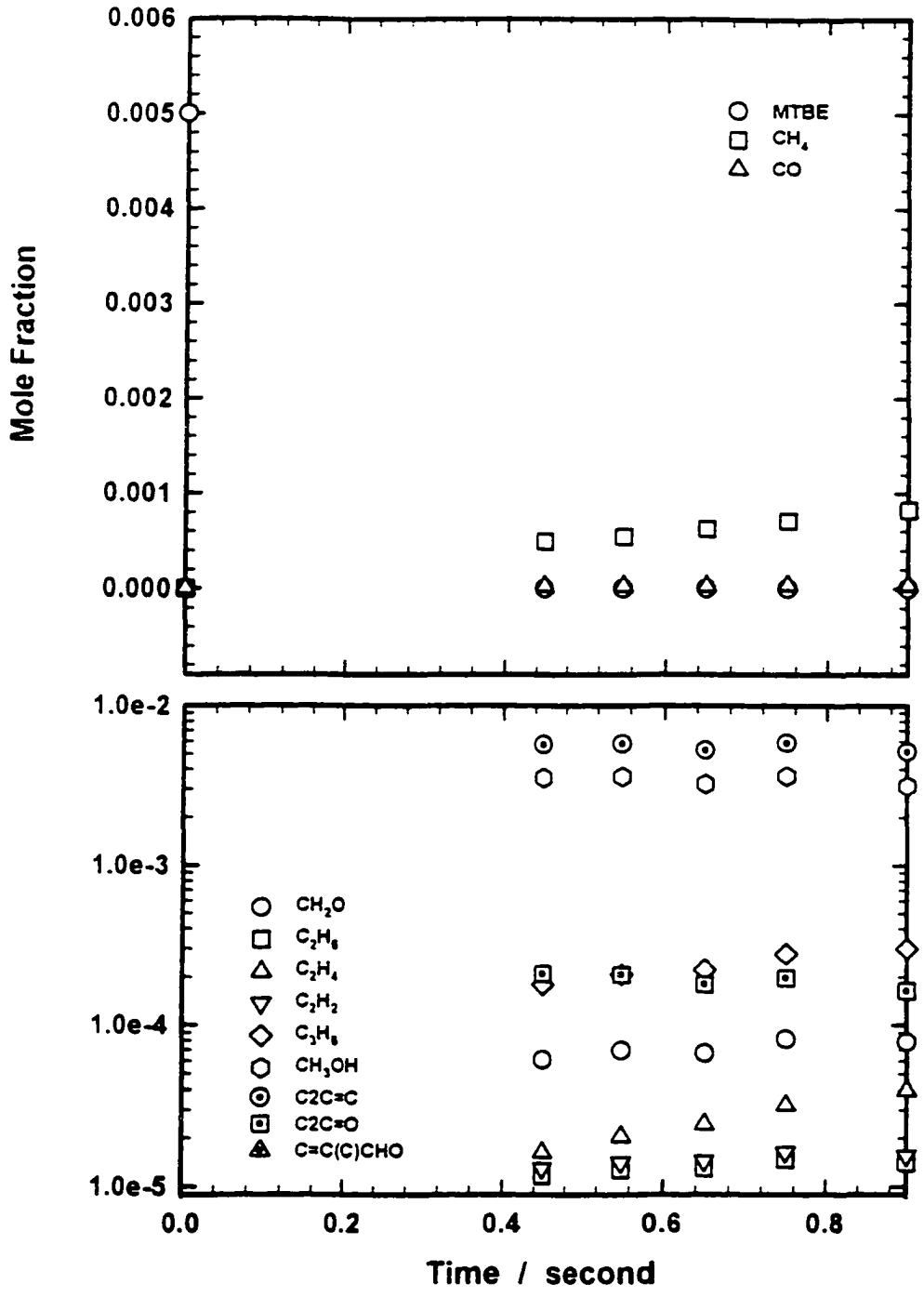


Figure IIC. 66 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 4 atm, T = 1023 K

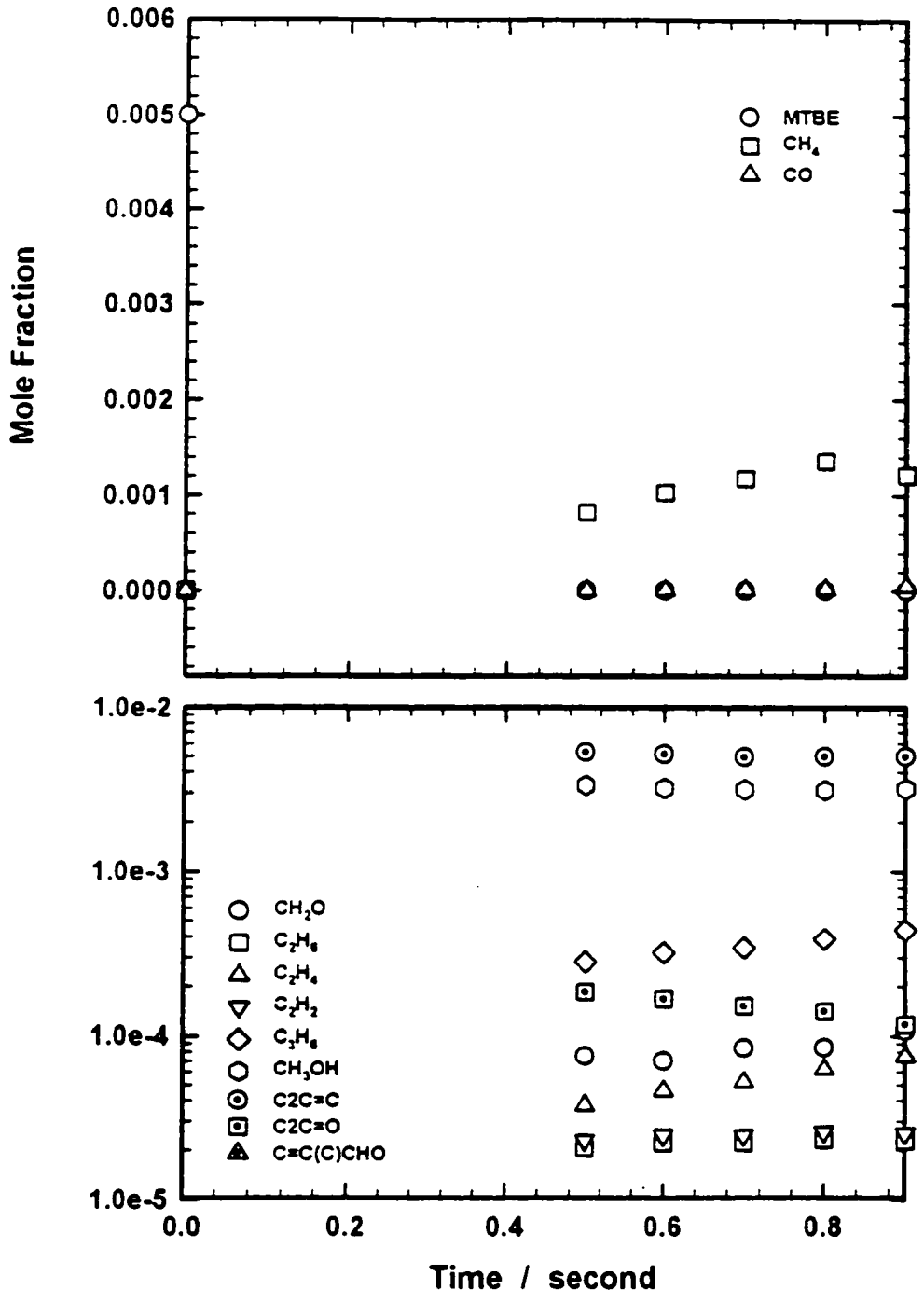


Figure IIC. 67 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 4 atm, T = 1048 K

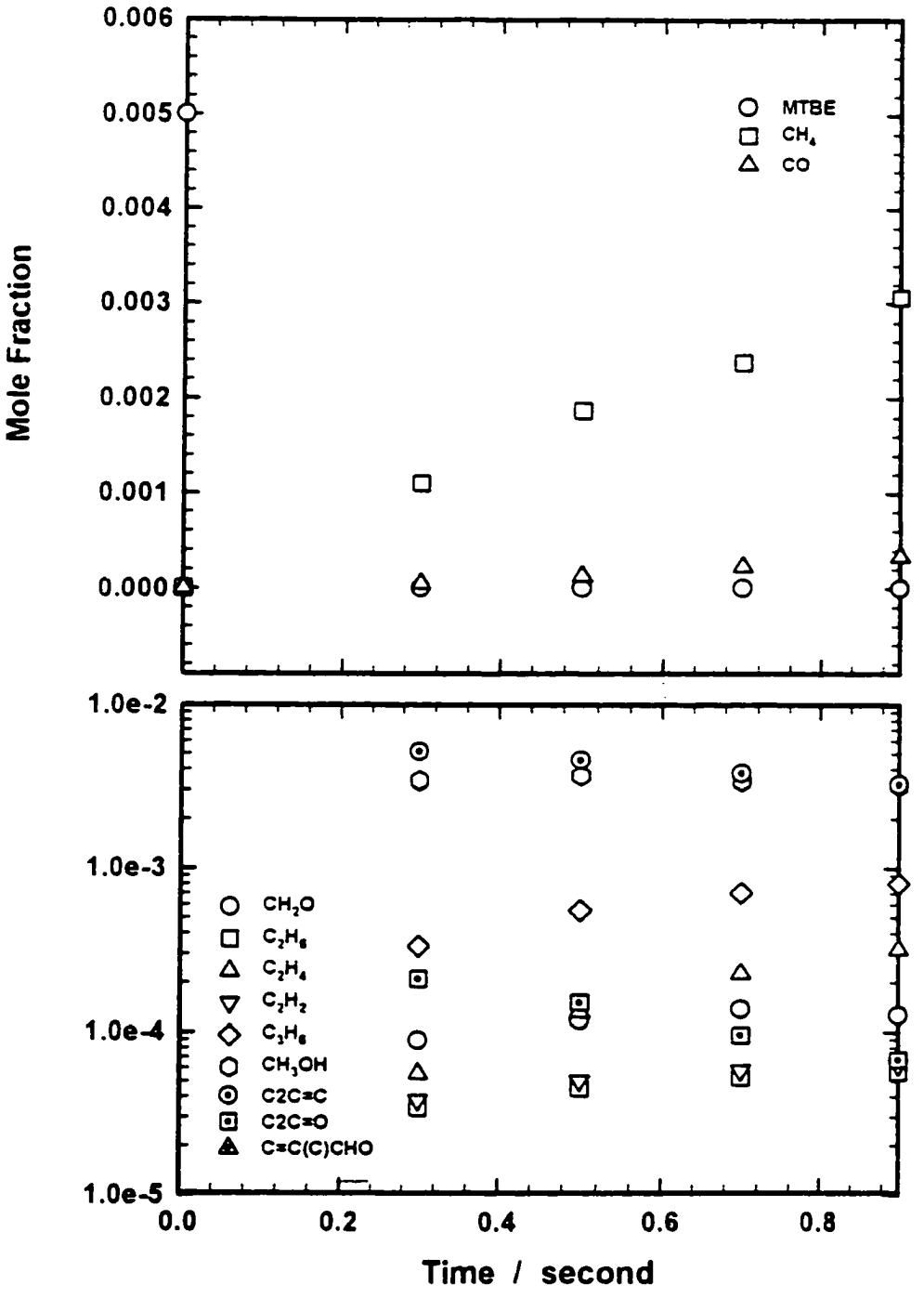


Figure IIC. 68 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 4 atm, T = 1073 K

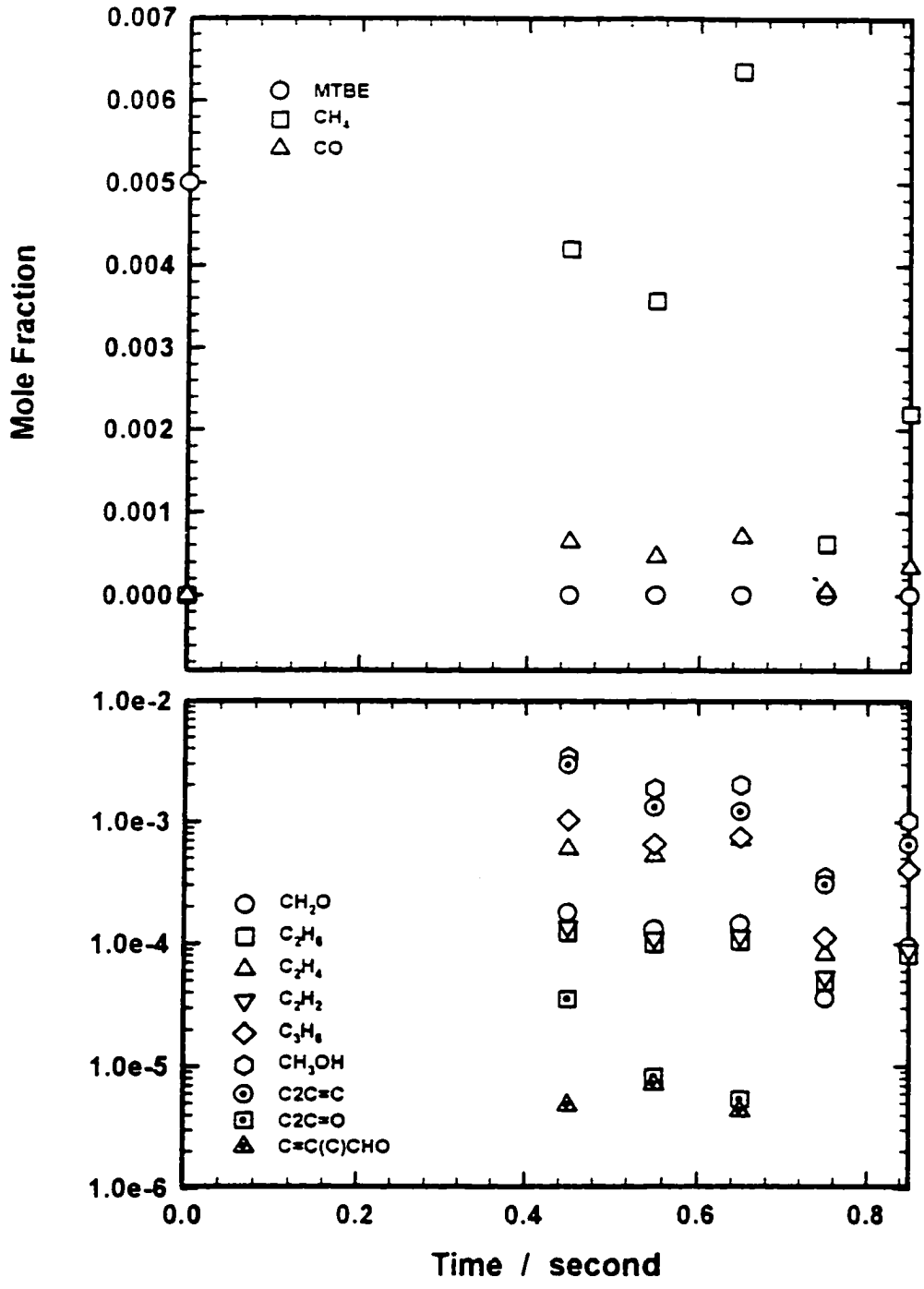


Figure IIC. 69 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 4 atm, T = 1123 K

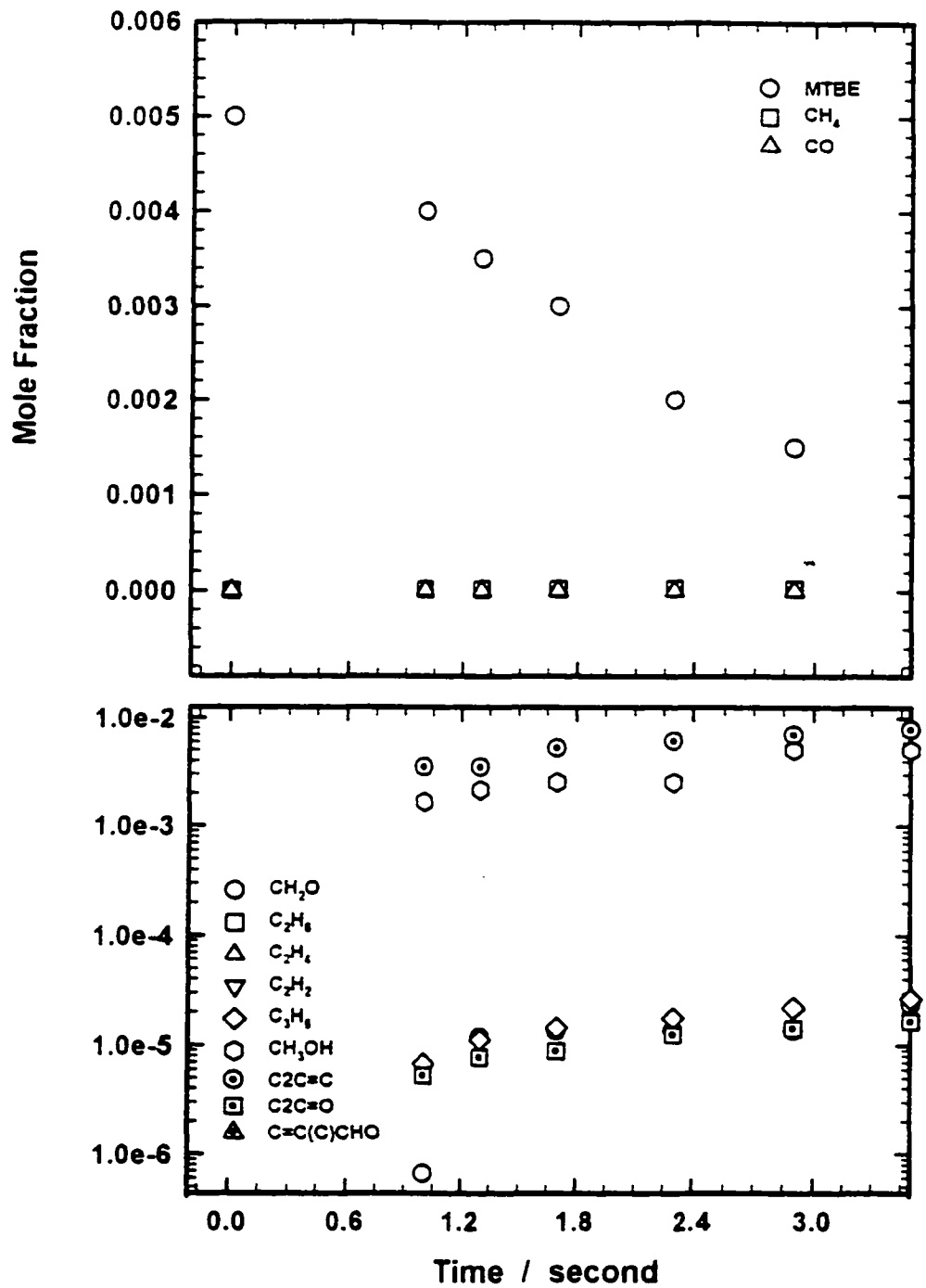


Figure IIC. 70 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 7 atm, T = 873 K

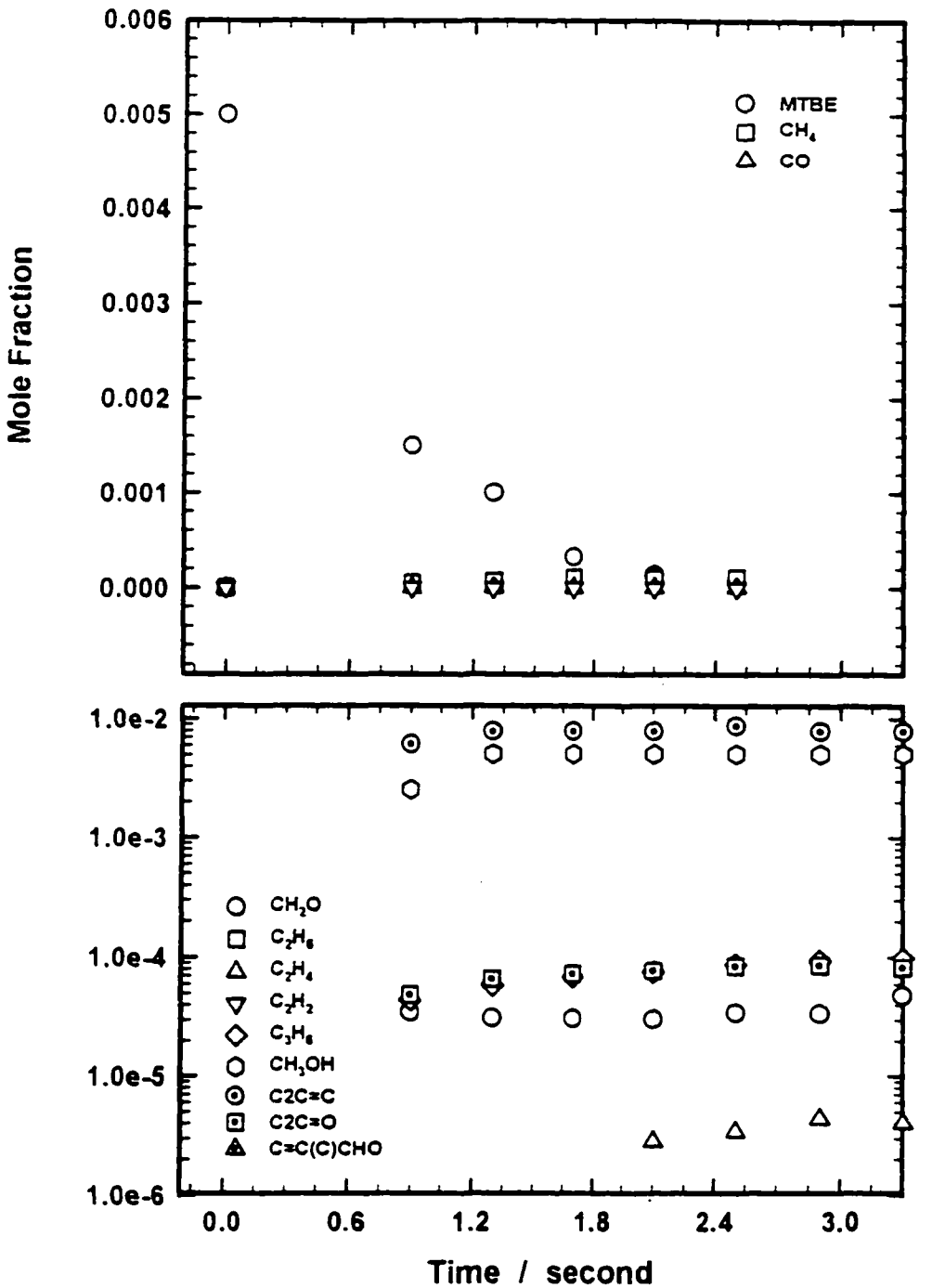


Figure IIC. 71 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 7 atm, T = 923 K

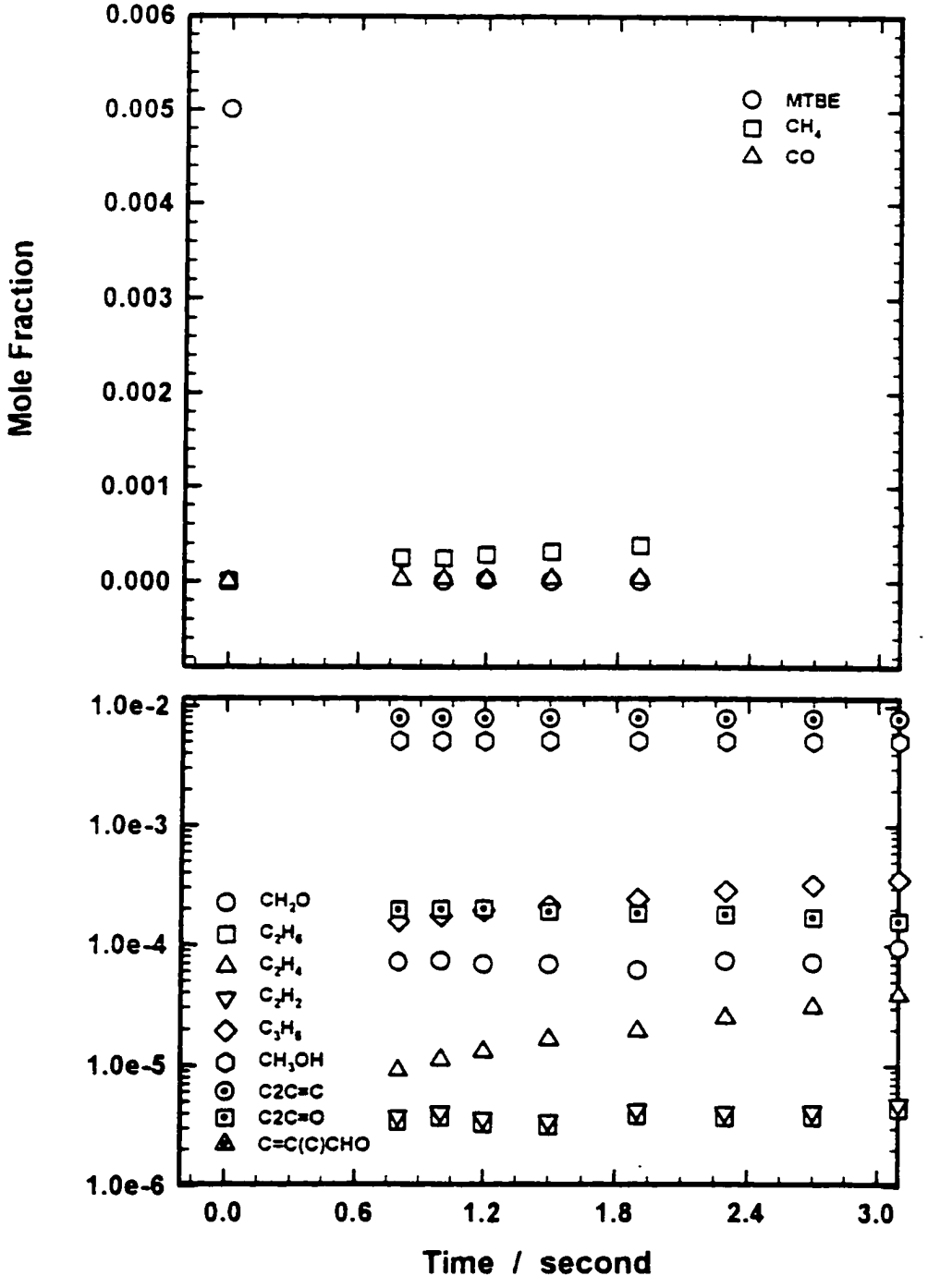


Figure IIC. 72 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 7 atm, T = 973 K

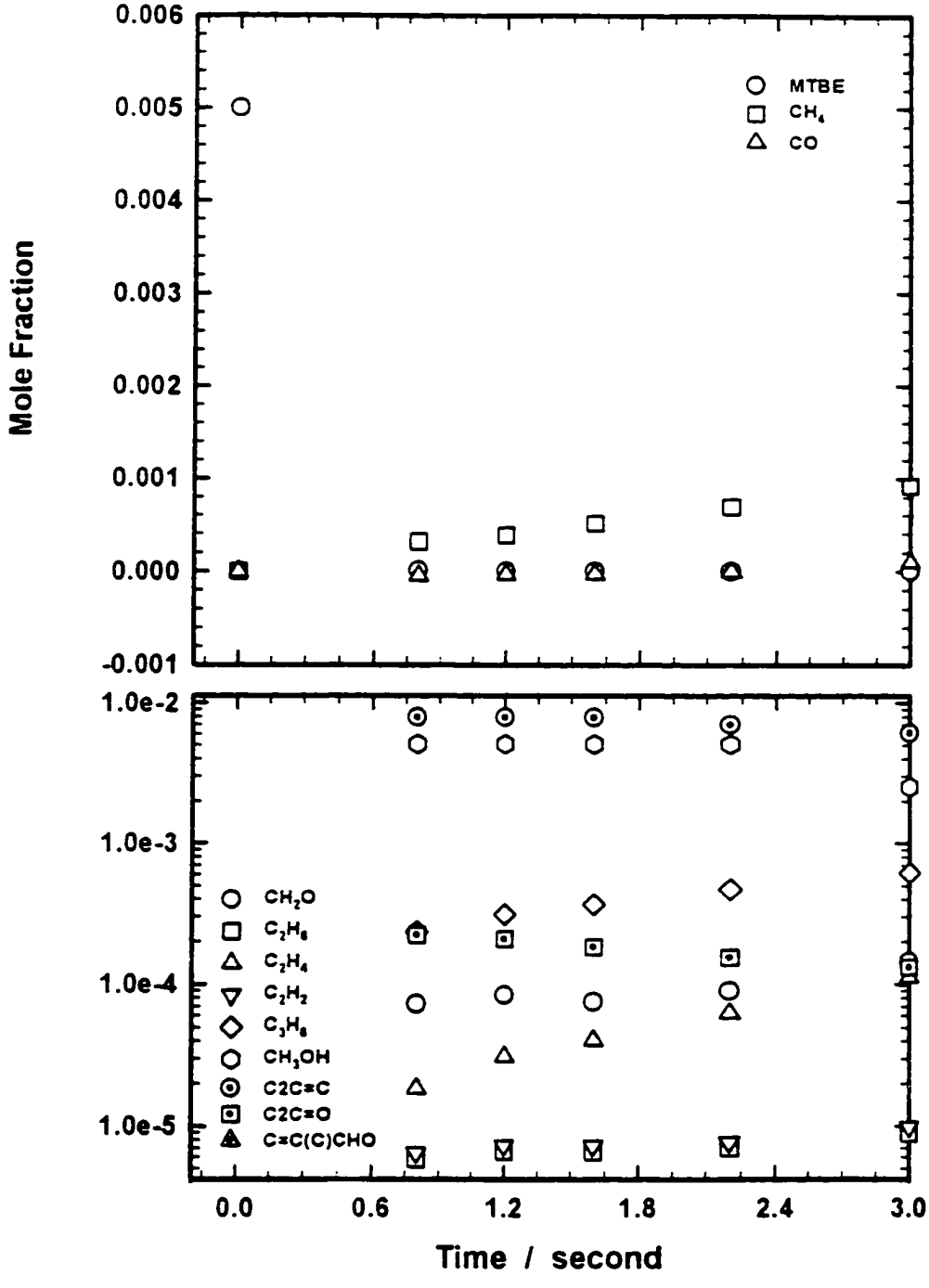


Figure IIC. 73 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 7 atm, T = 998 K

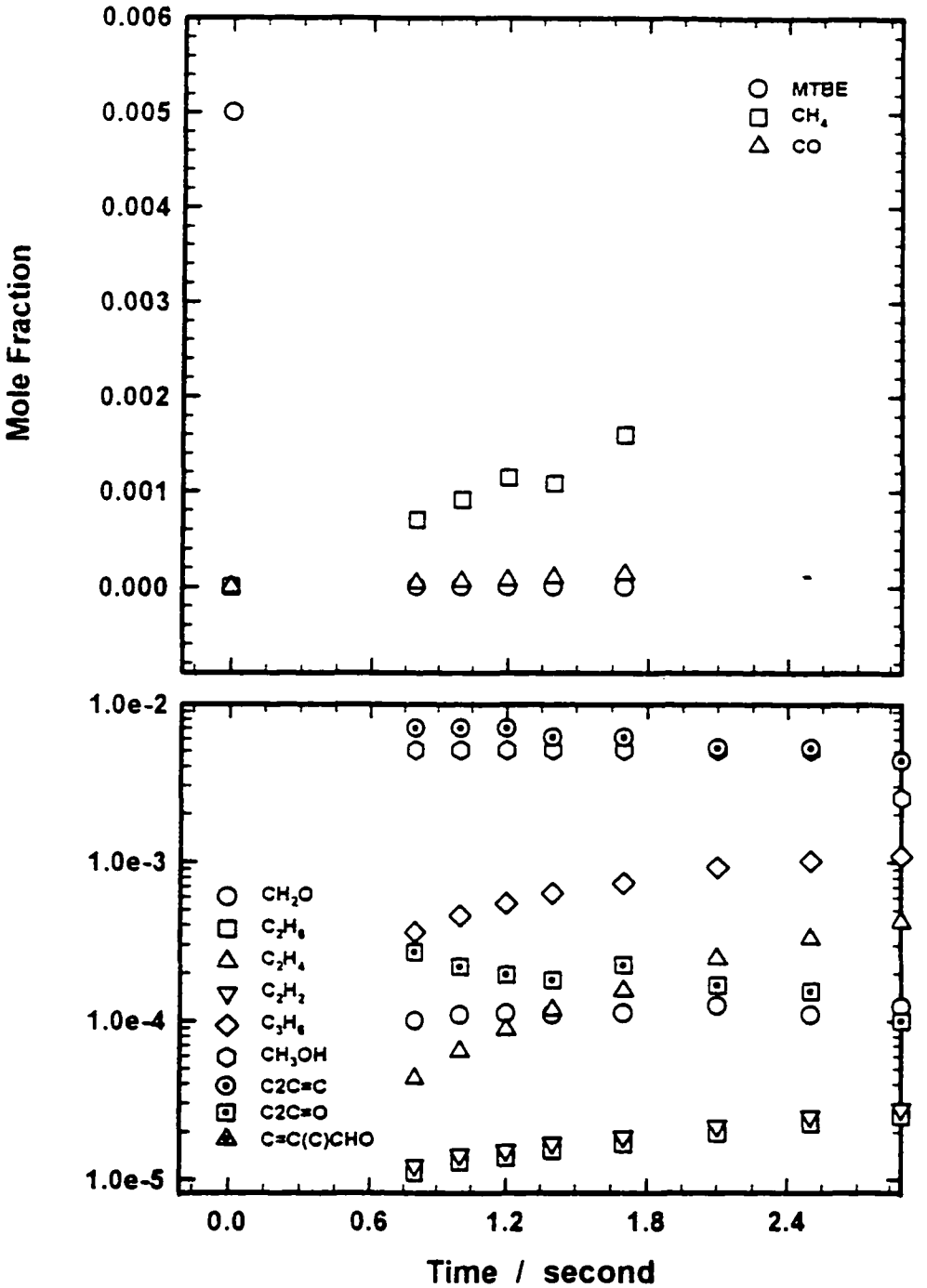


Figure IIC. 74 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 7 atm, T = 1023 K

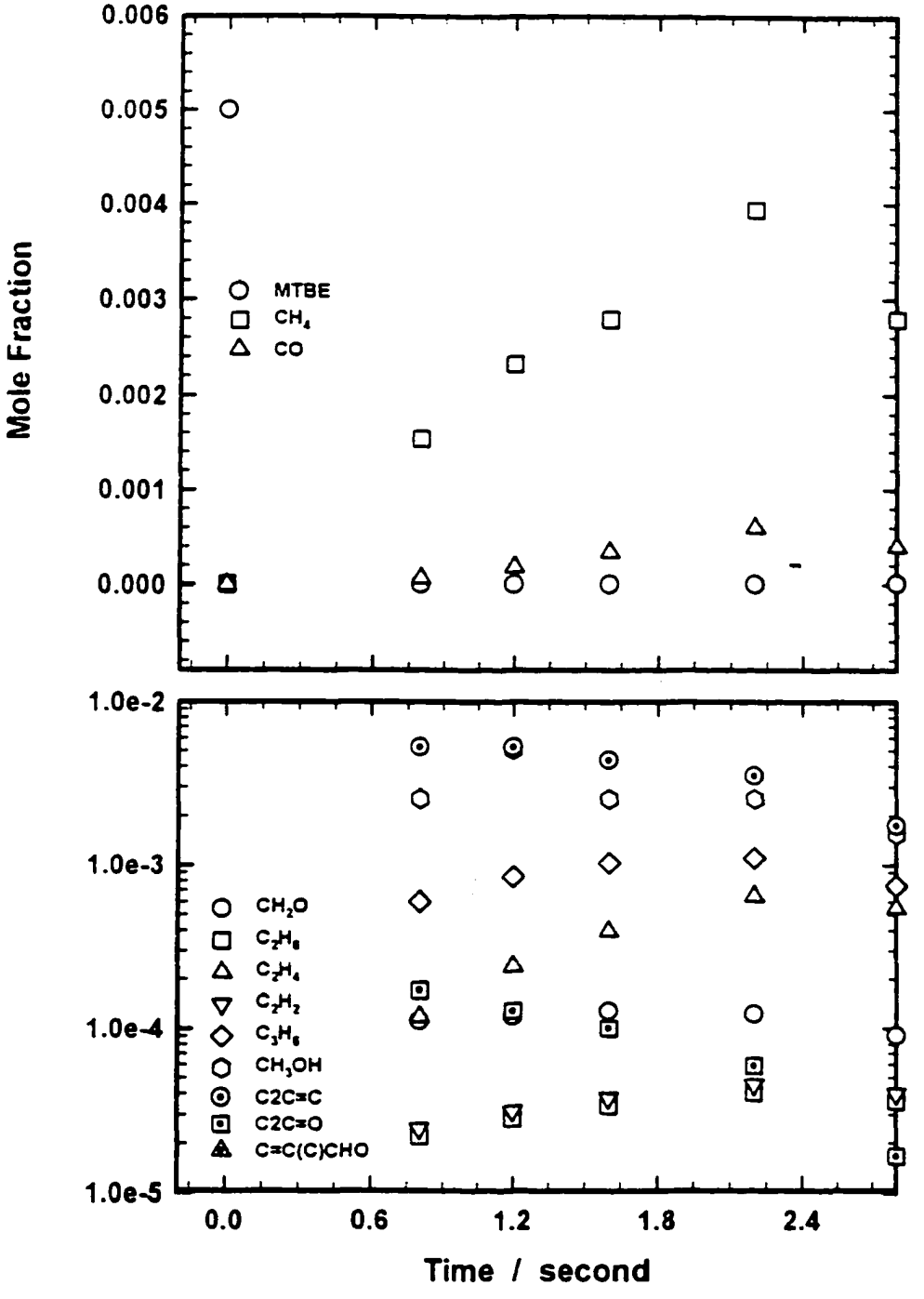


Figure IIC. 75 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 7 atm, T = 1048 K

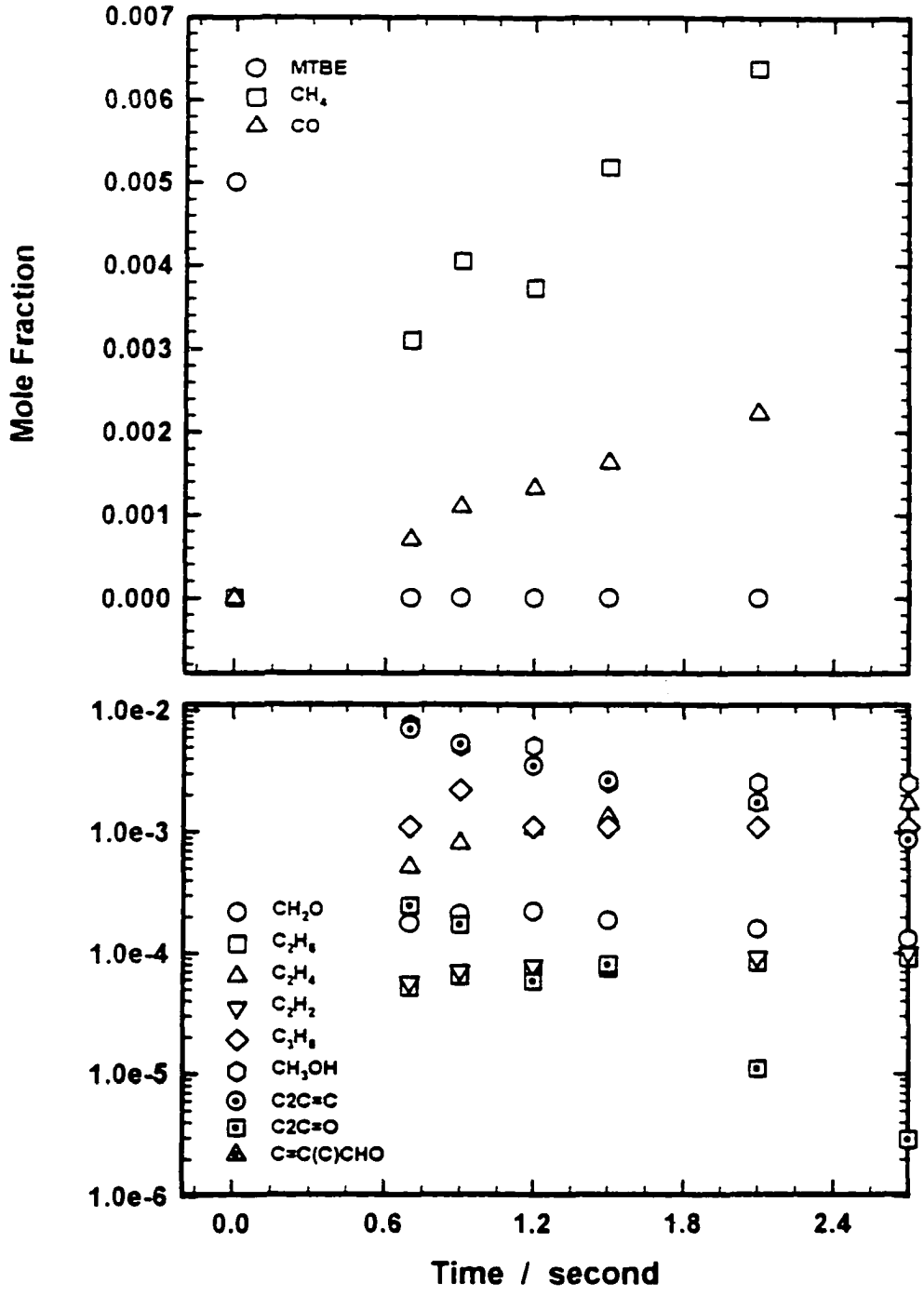


Figure IIC. 76 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 7 atm, T = 1073 K

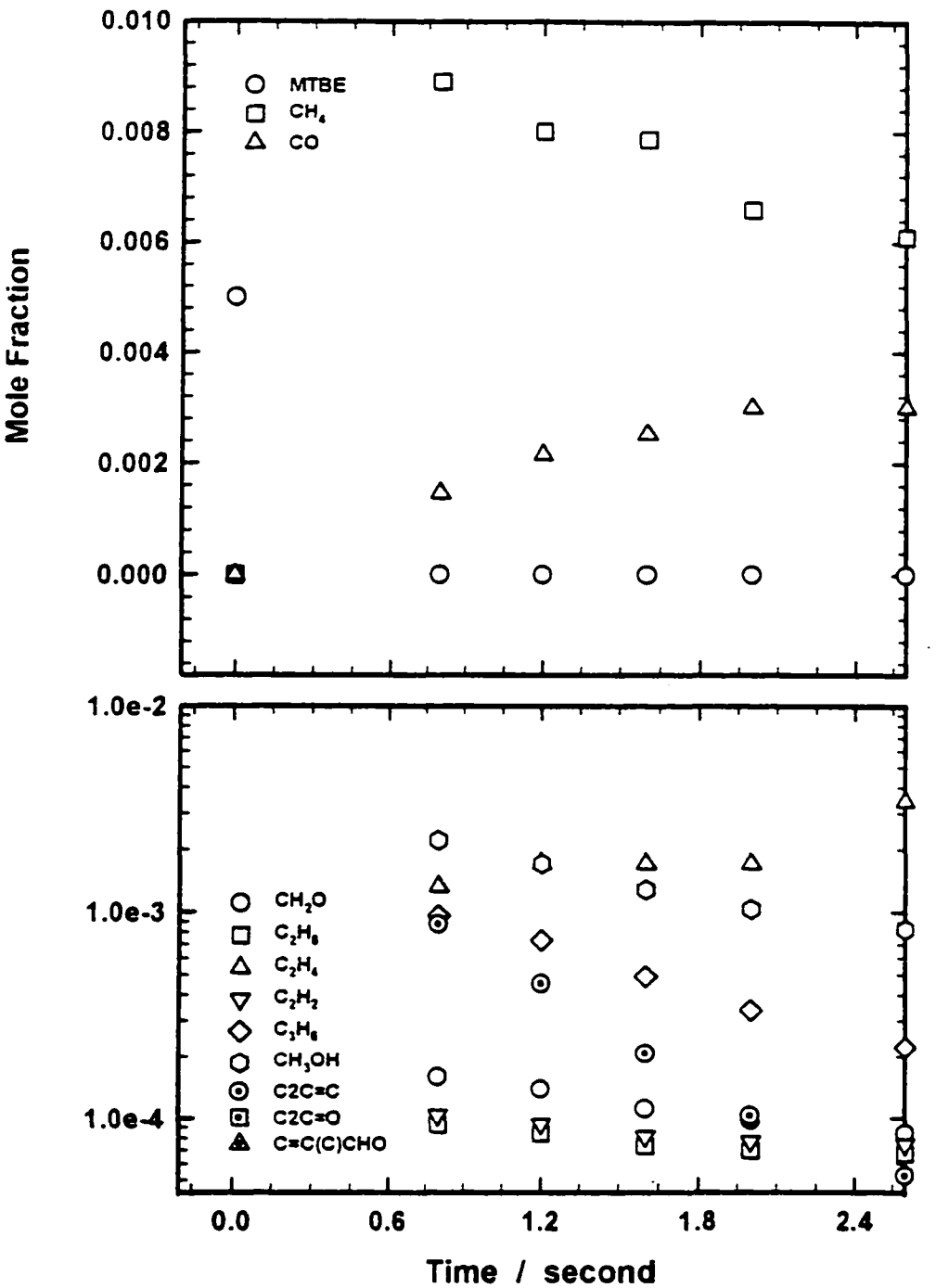


Figure IIC. 77 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 7 atm, T = 1123 K

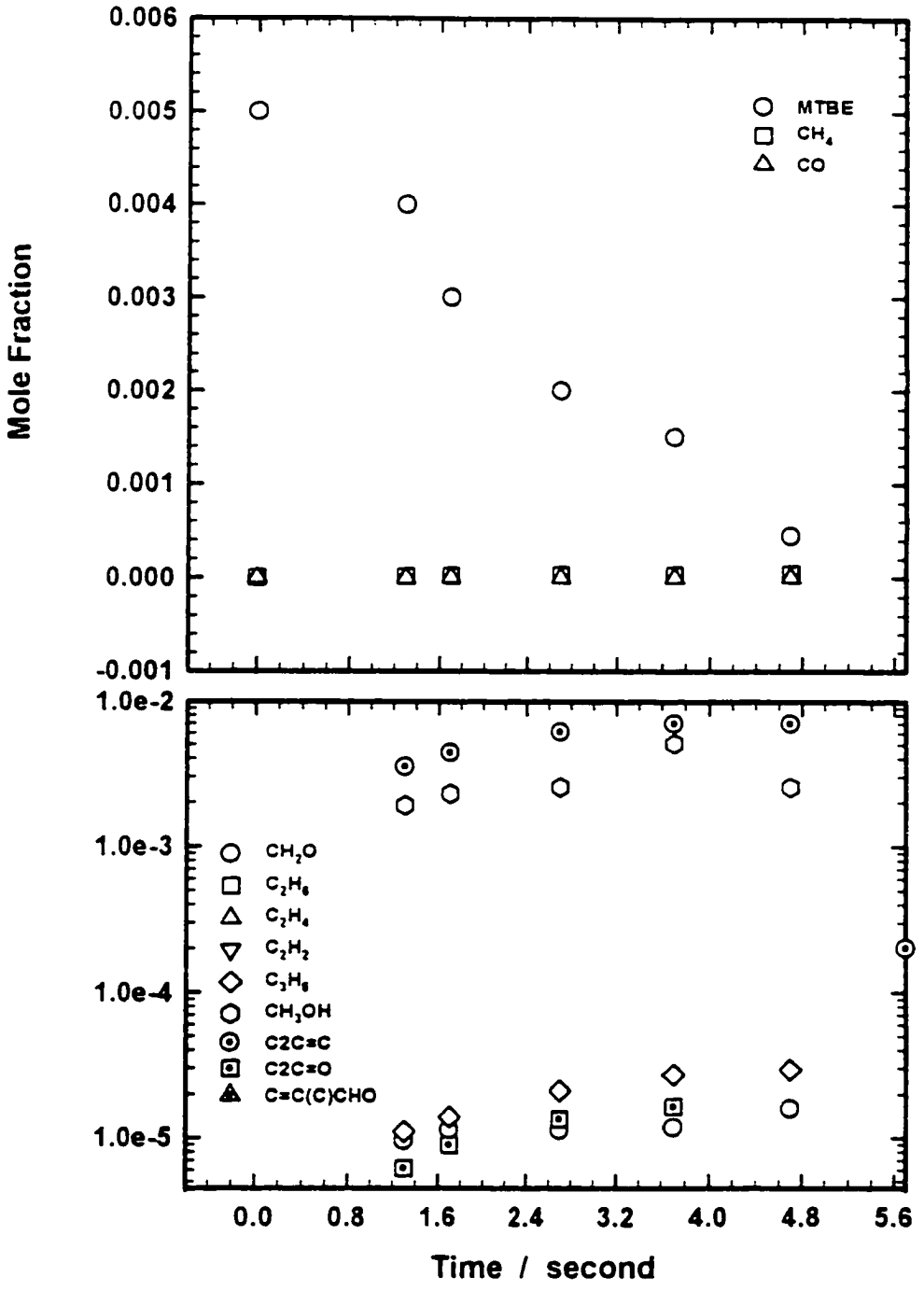


Figure IIC. 78 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 10 atm, T = 873 K

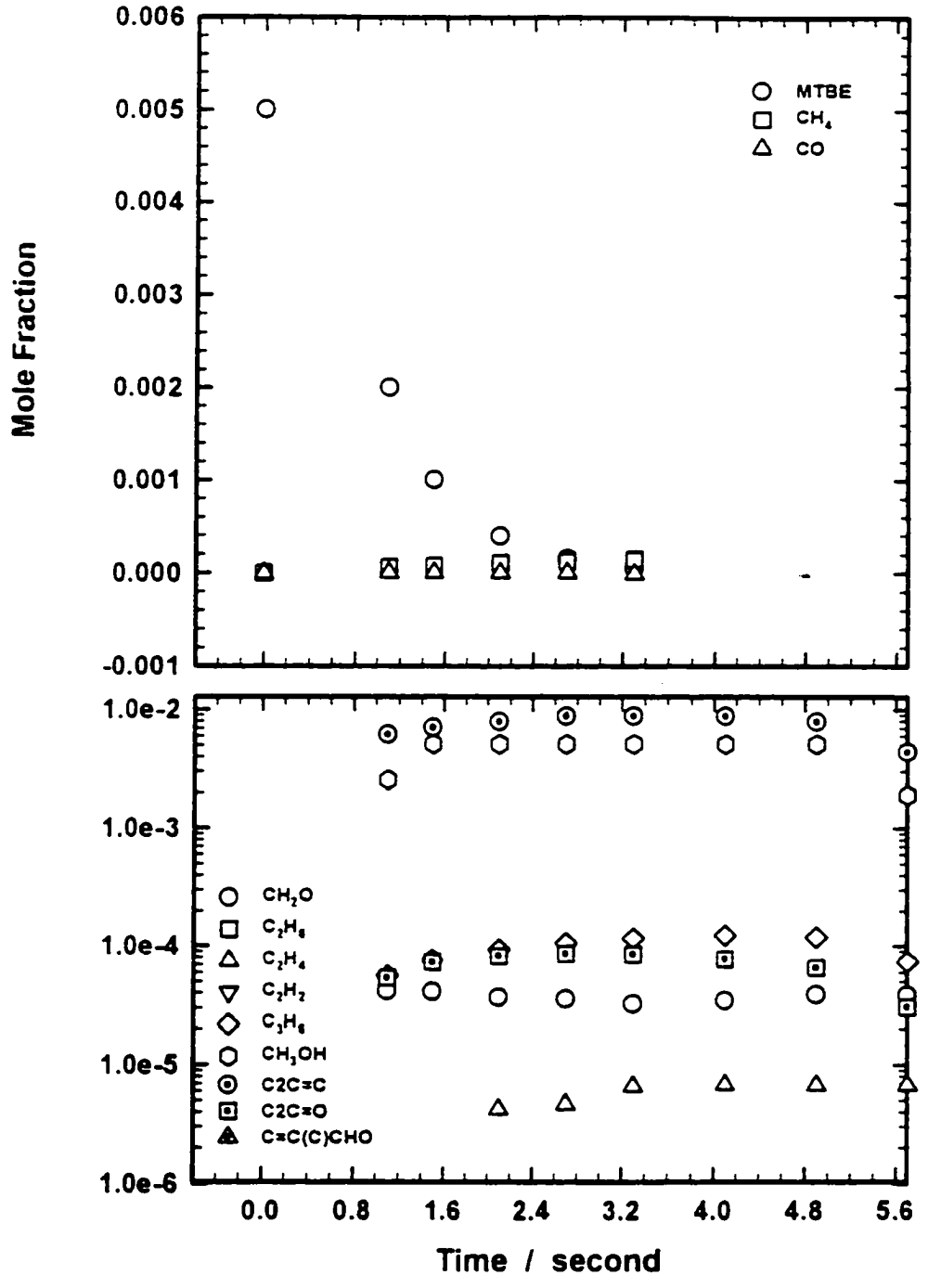


Figure IIC. 79 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 10 atm, T = 923 K

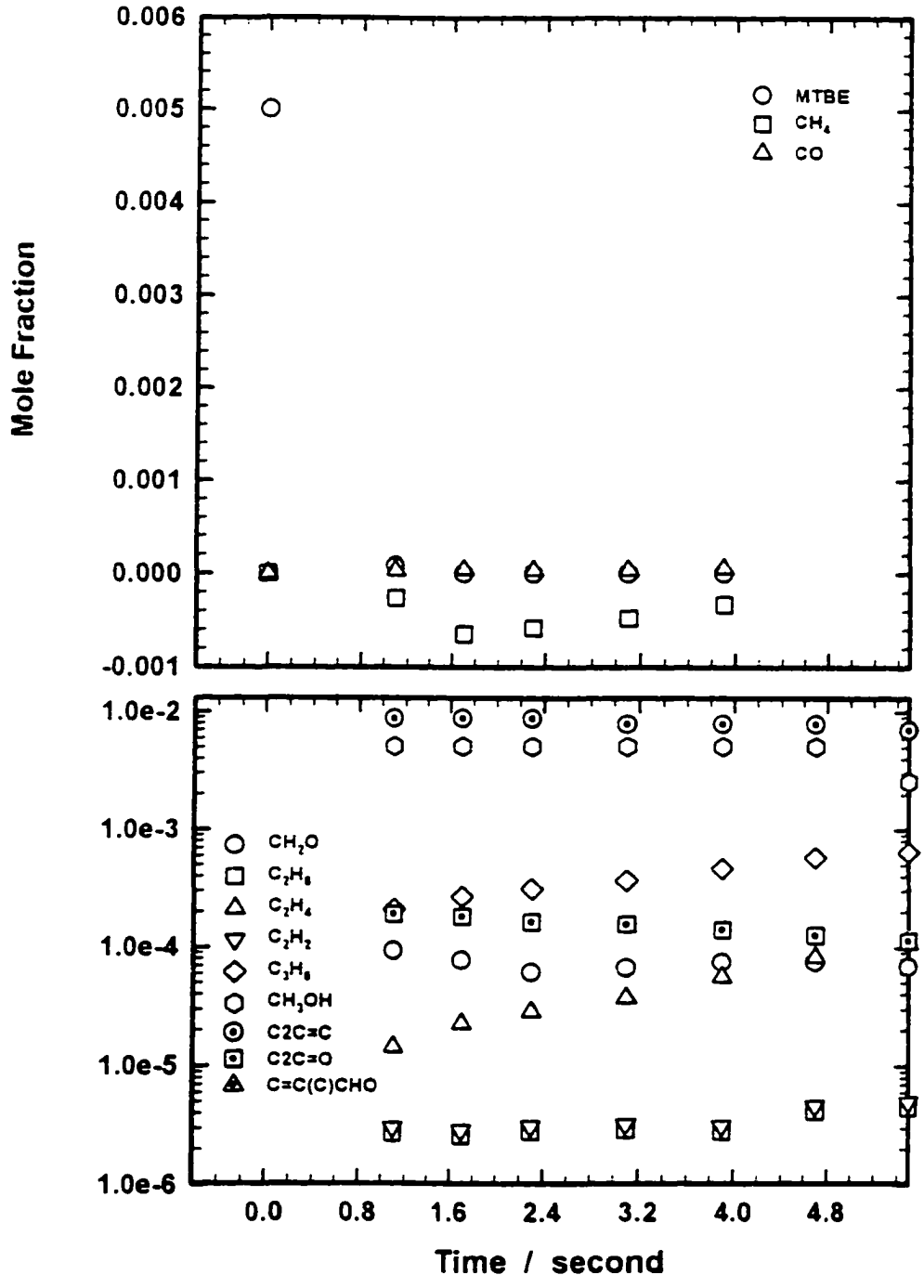


Figure IIC. 80 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 10 atm, T = 973 K

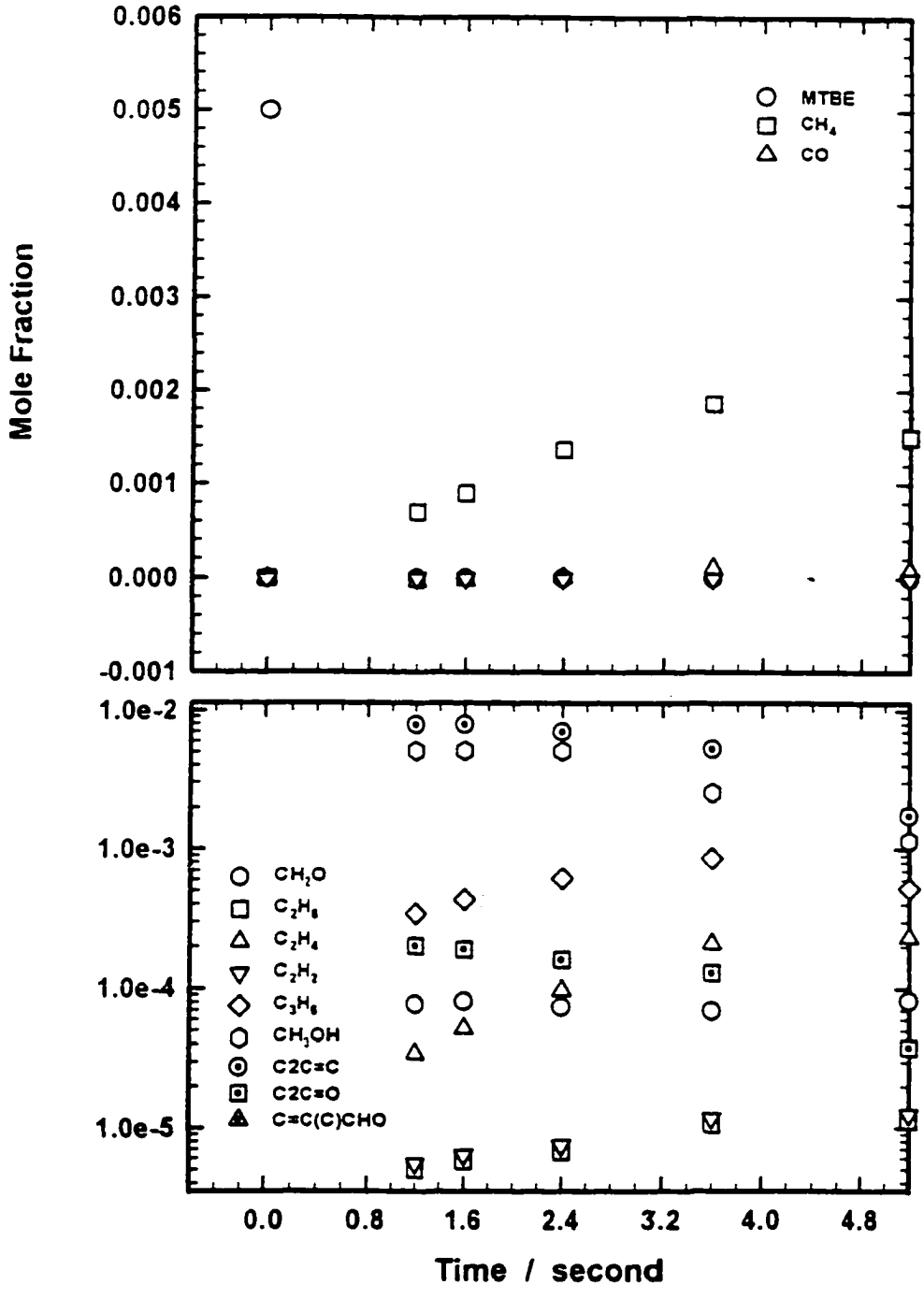


Figure IIC. 81 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 10 atm, T = 998 K

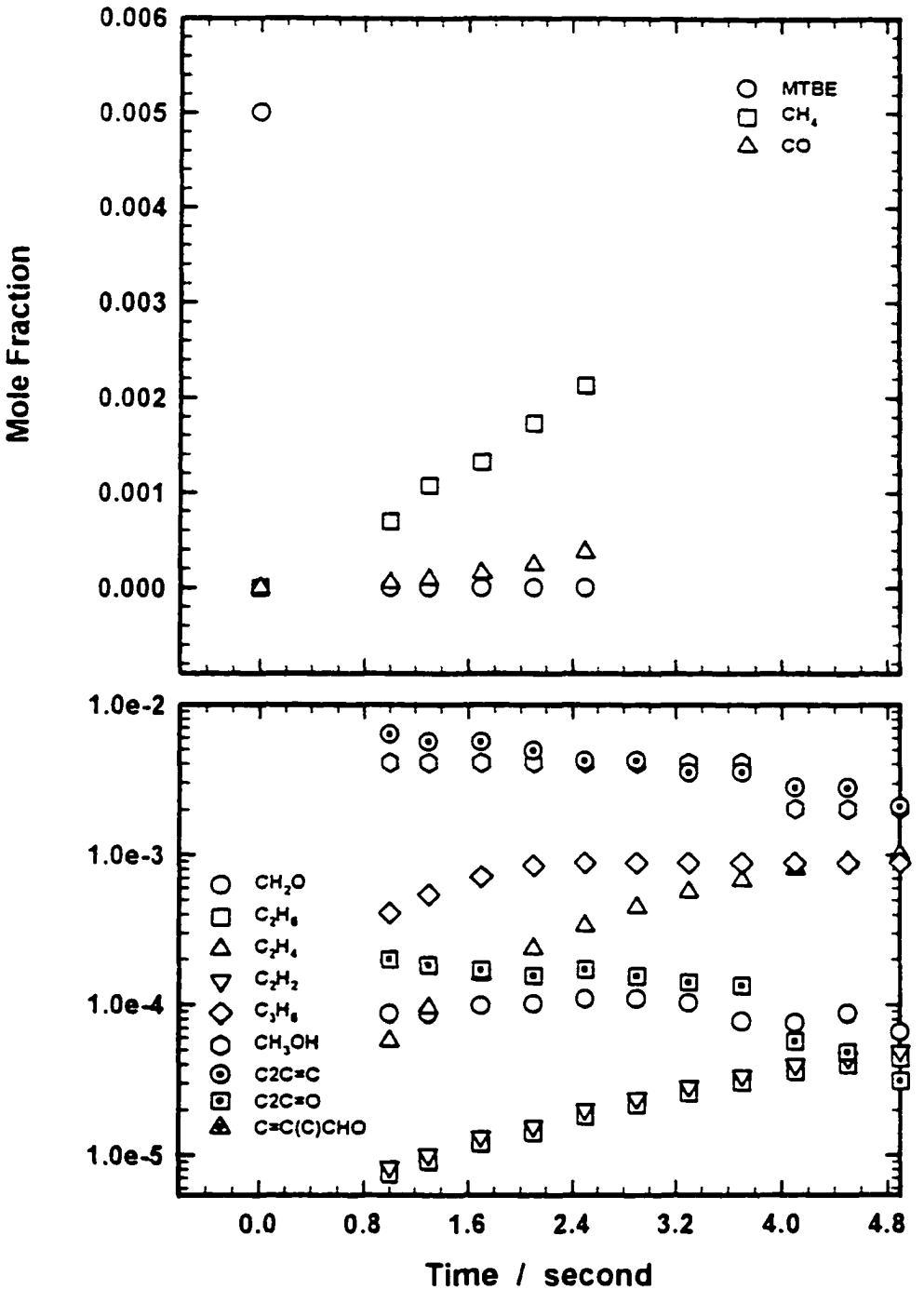


Figure IIC. 82 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 10 atm, T = 1023 K

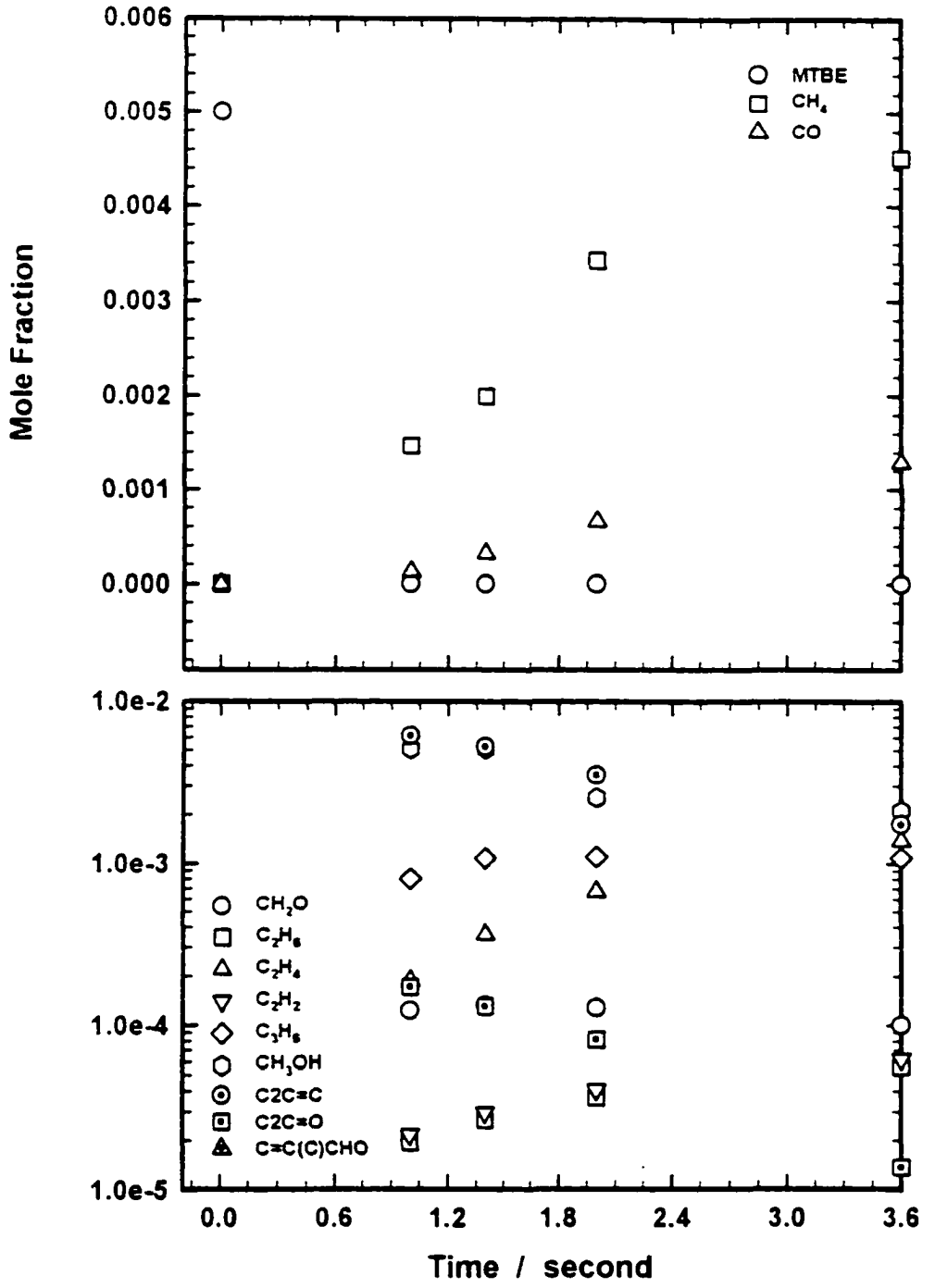


Figure ПС. 83 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 10 atm, T = 1048 K

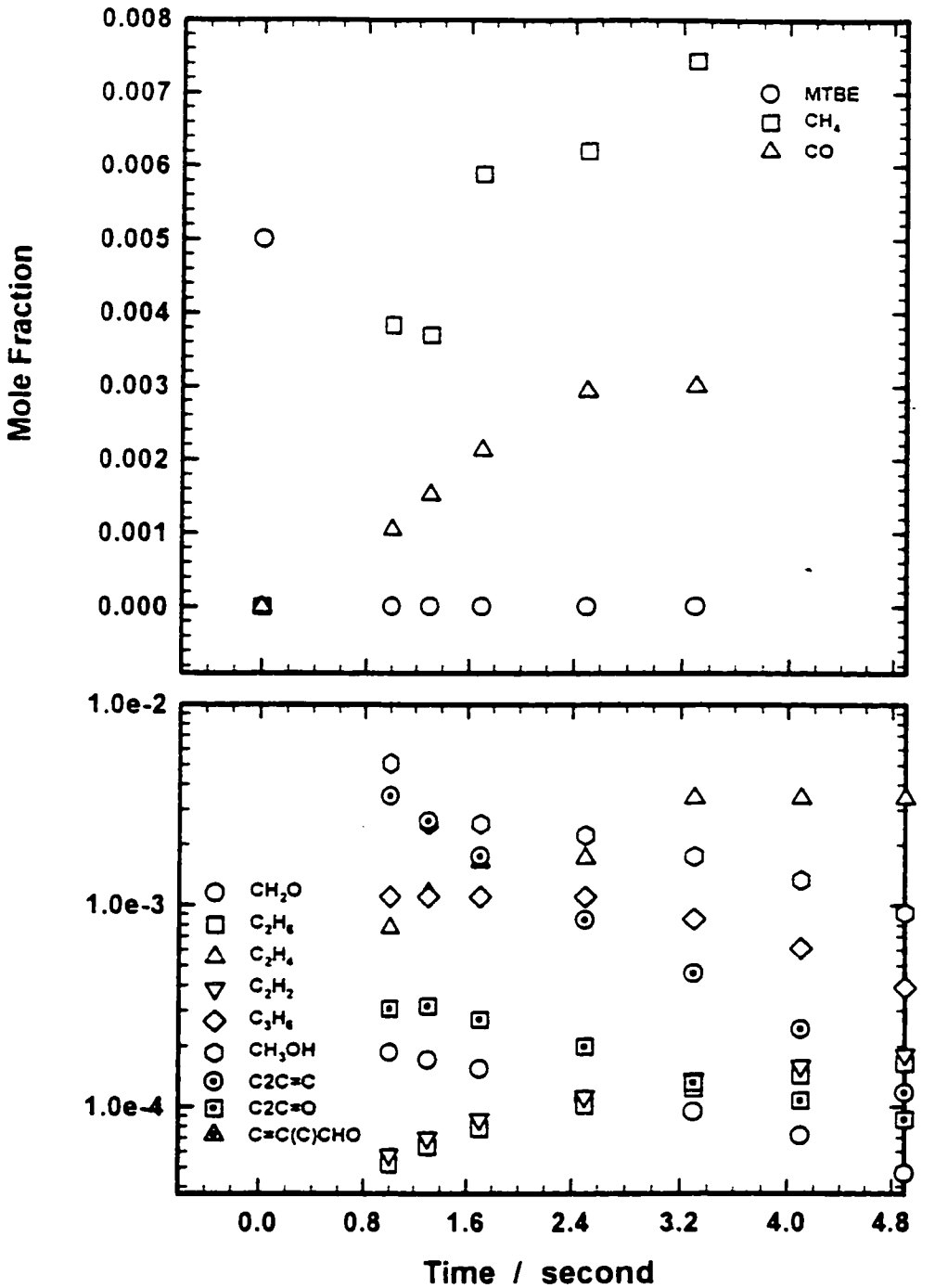


Figure IIC. 84 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 10 atm, T = 1073 K

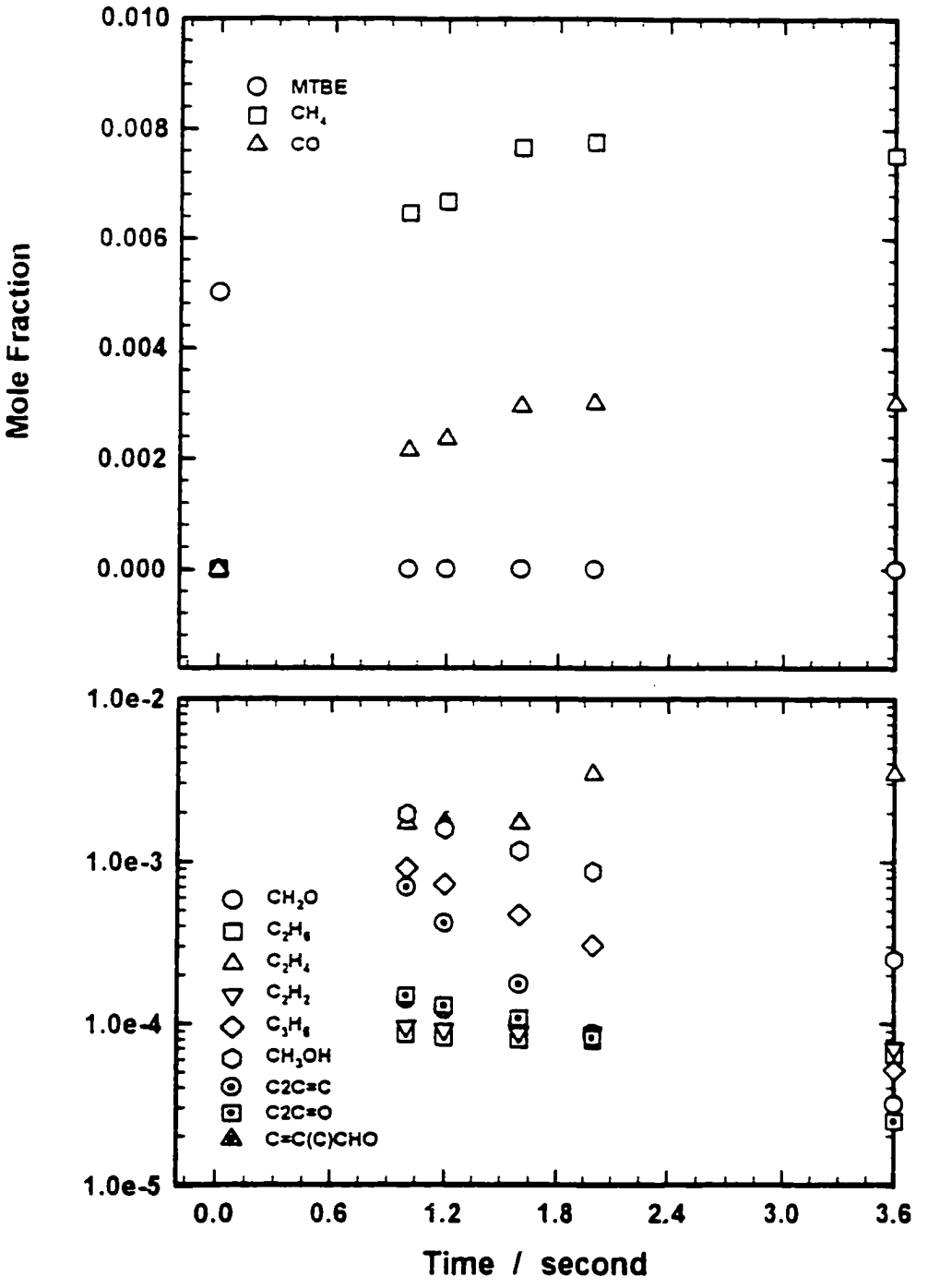


Figure IIC. 85 Experimental result of 0.5% MTBE pyrolysis product distribution at P = 10 atm, T = 1123 K

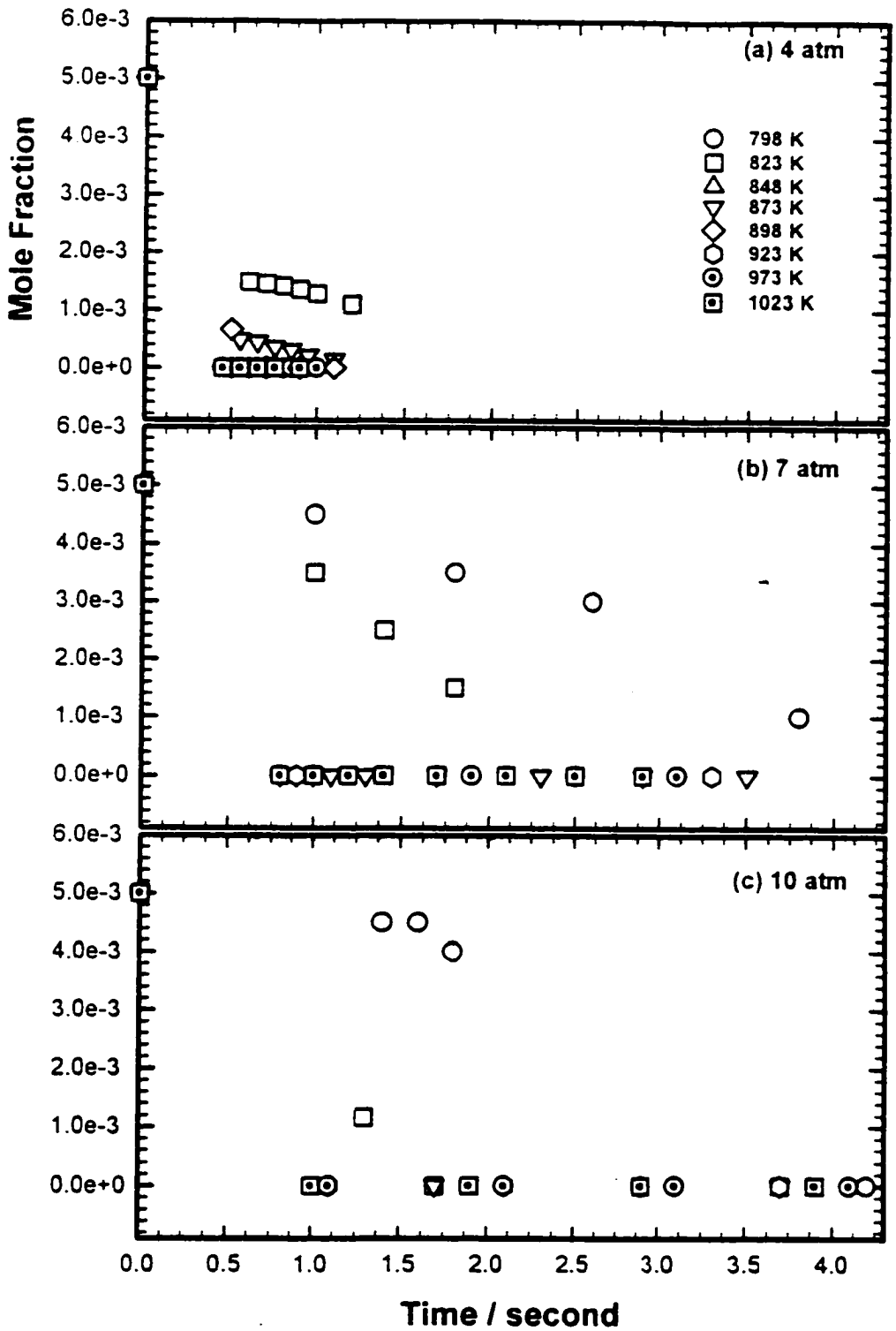


Figure IIC. 86 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of MTBE at $\varphi = 0.75$

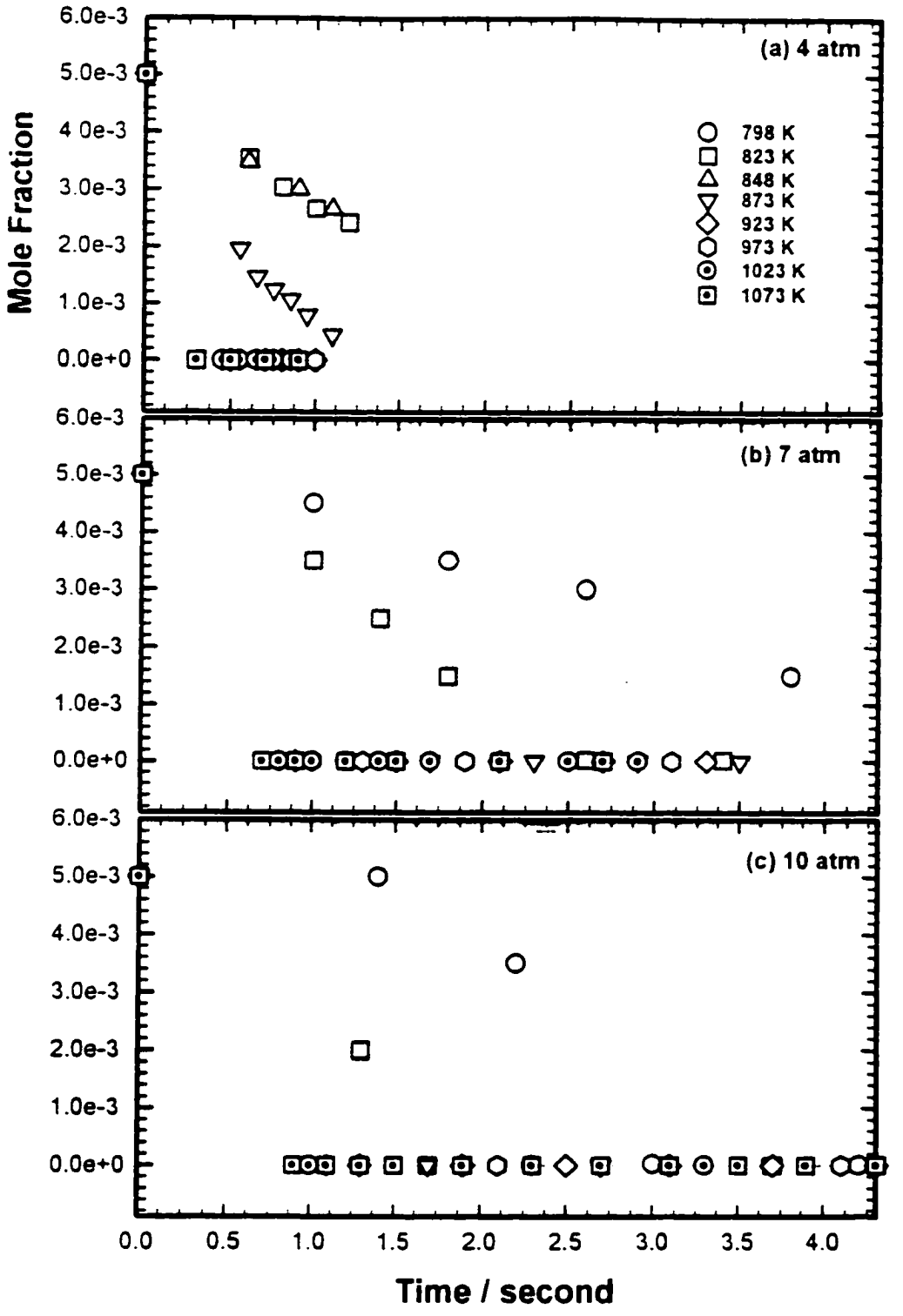


Figure IIC. 87 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of MTBE at $\varphi = 1.00$

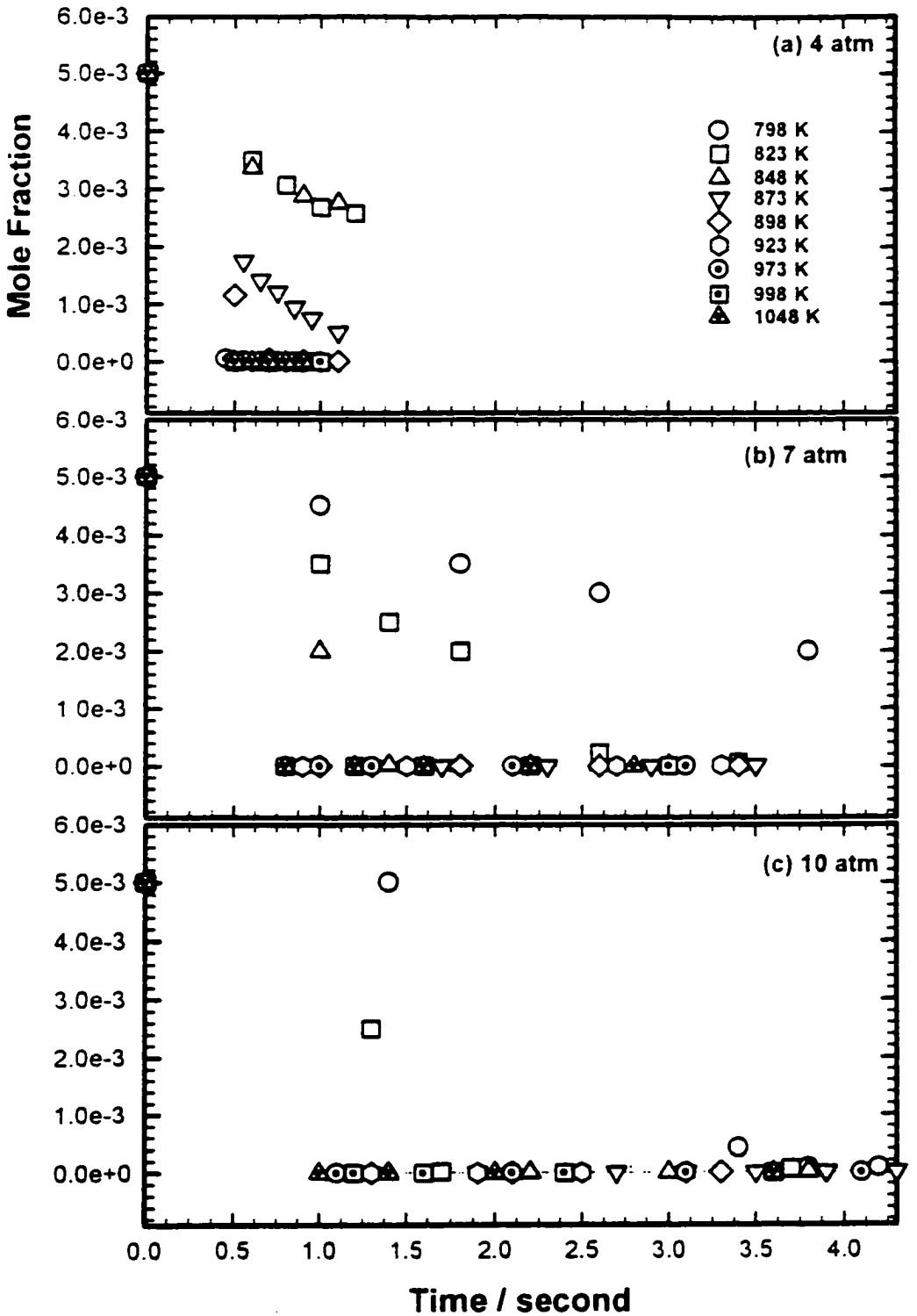


Figure IIC. 88 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of MTBE at φ = 1.50

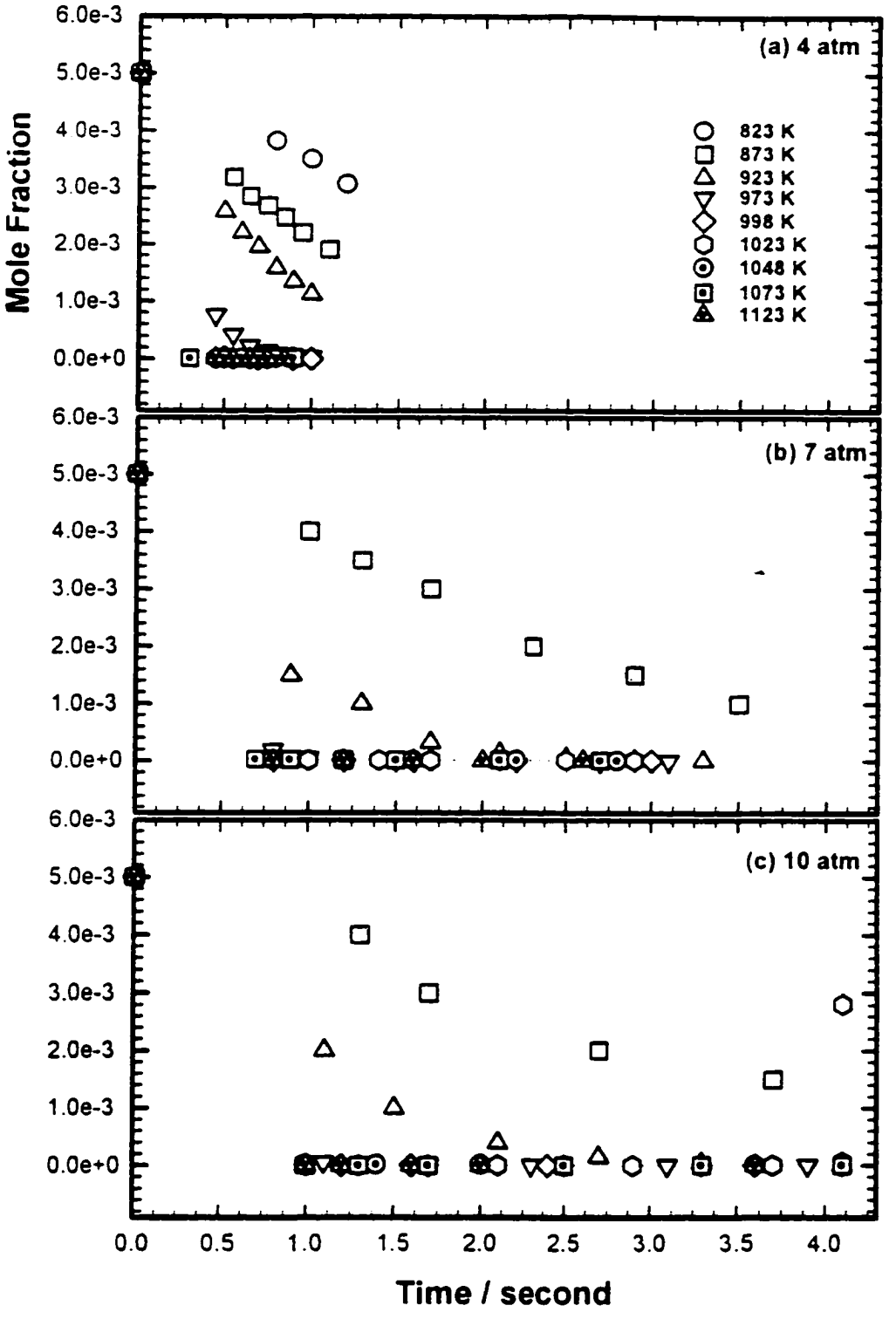


Figure IIC. 89 Experimental result of 0.5% MTBE pyrolysis: temperature and pressure dependence of MTBE

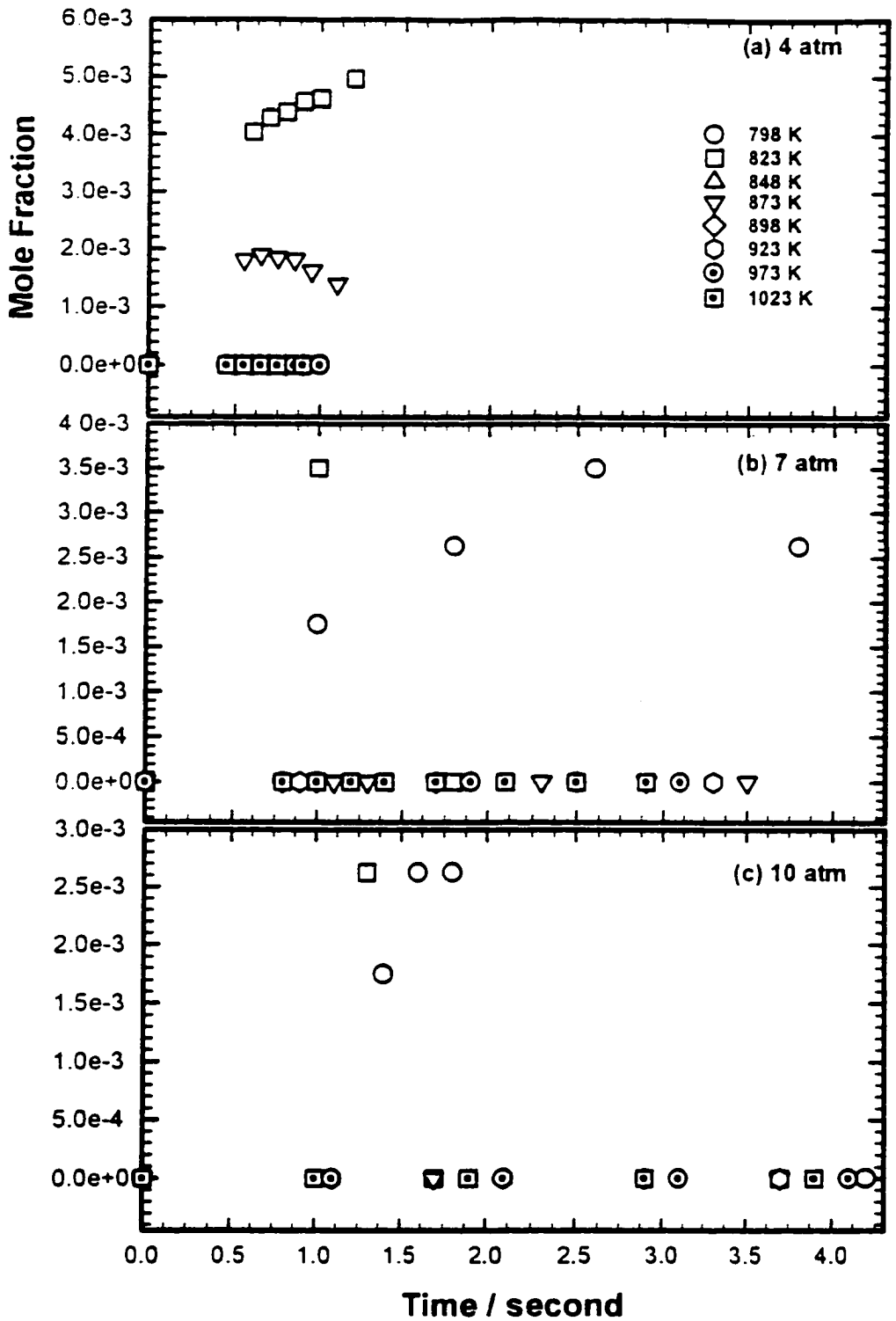


Figure IIC. 90 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of $C_2C{=}C$ at $\varphi = 0.75$

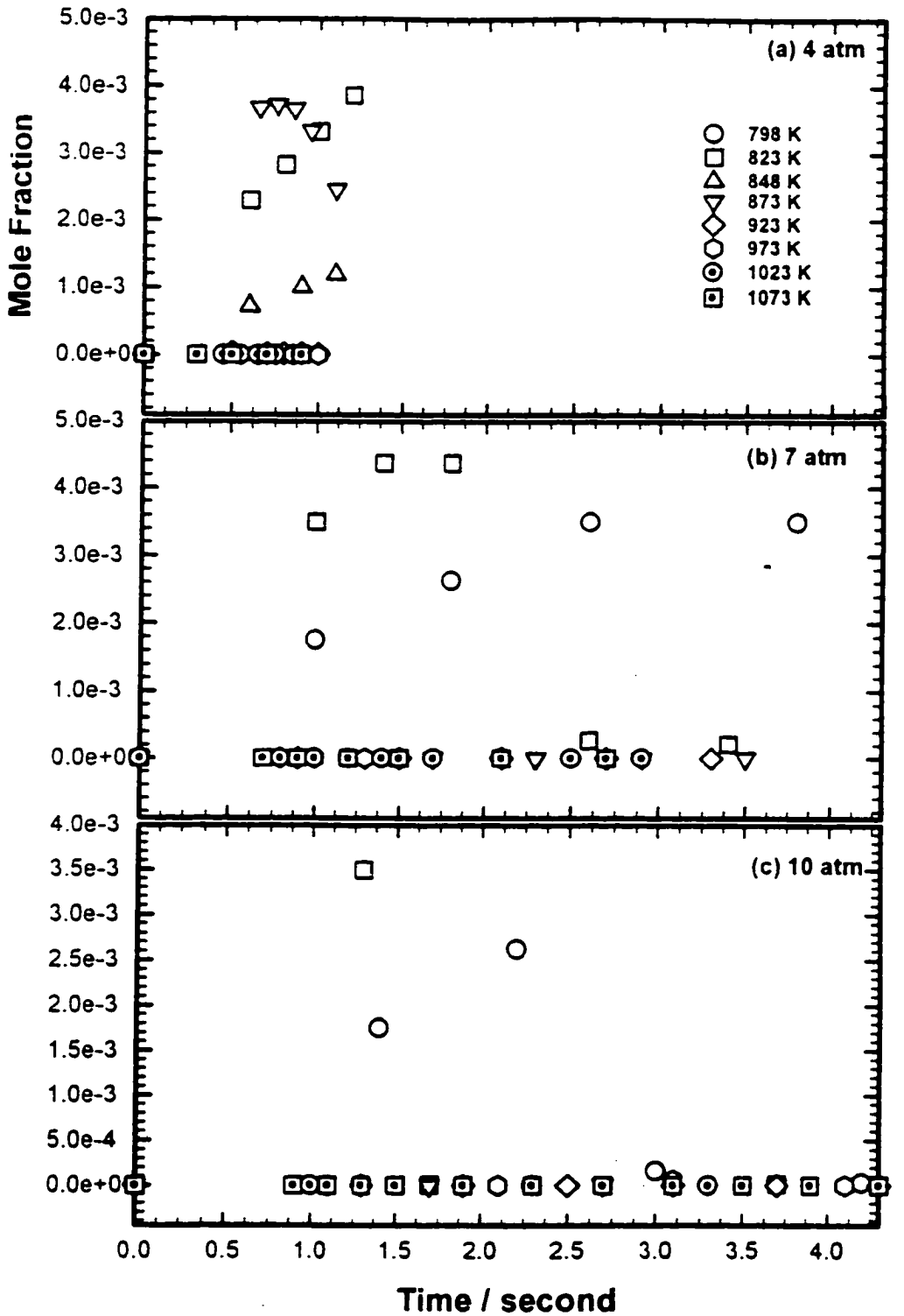


Figure IIC. 91 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of $C_2C{=}C$ at $\varphi = 1.00$

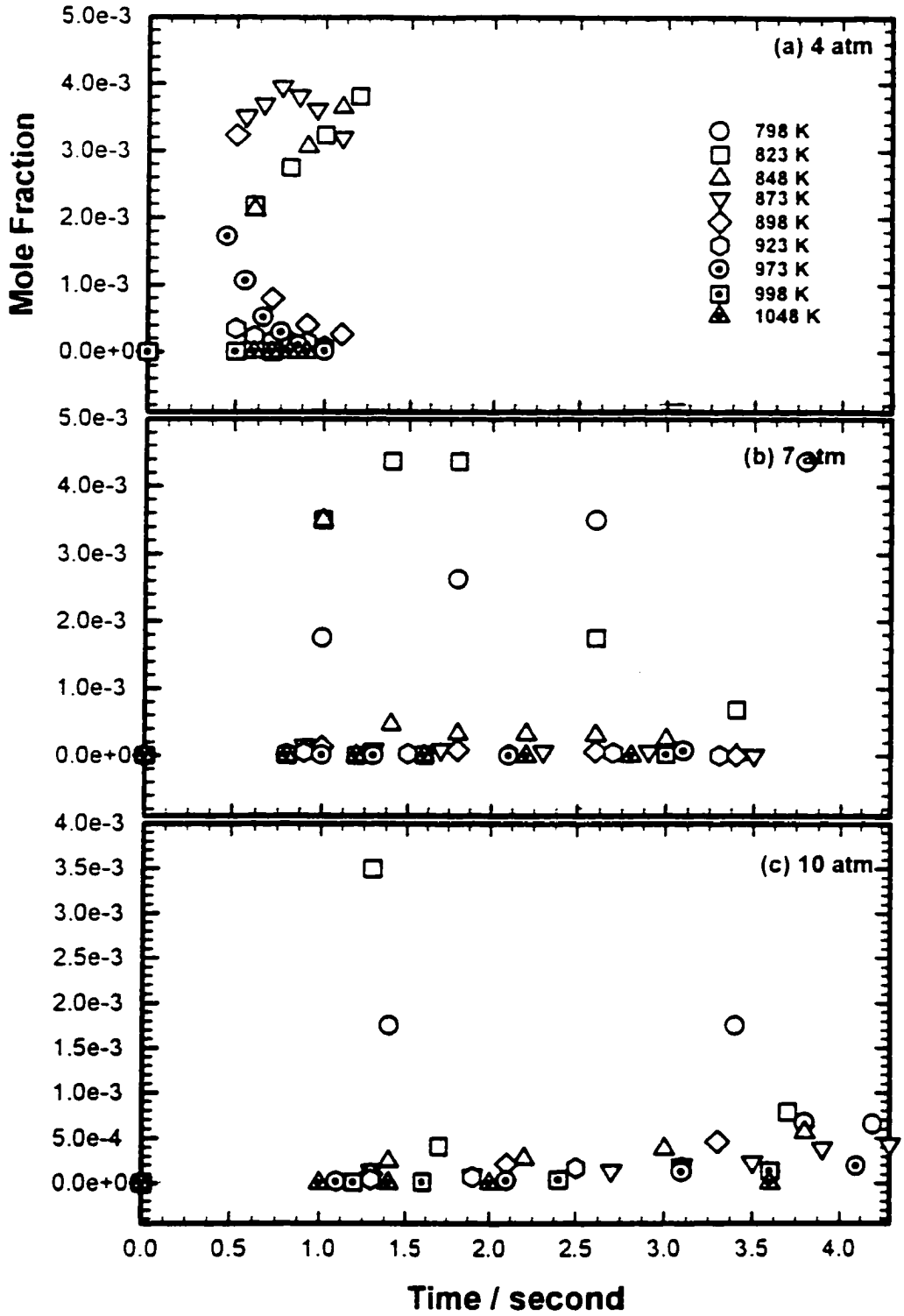


Figure IIC. 92 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of $C_2C{=}C$ at $\varphi = 1.50$

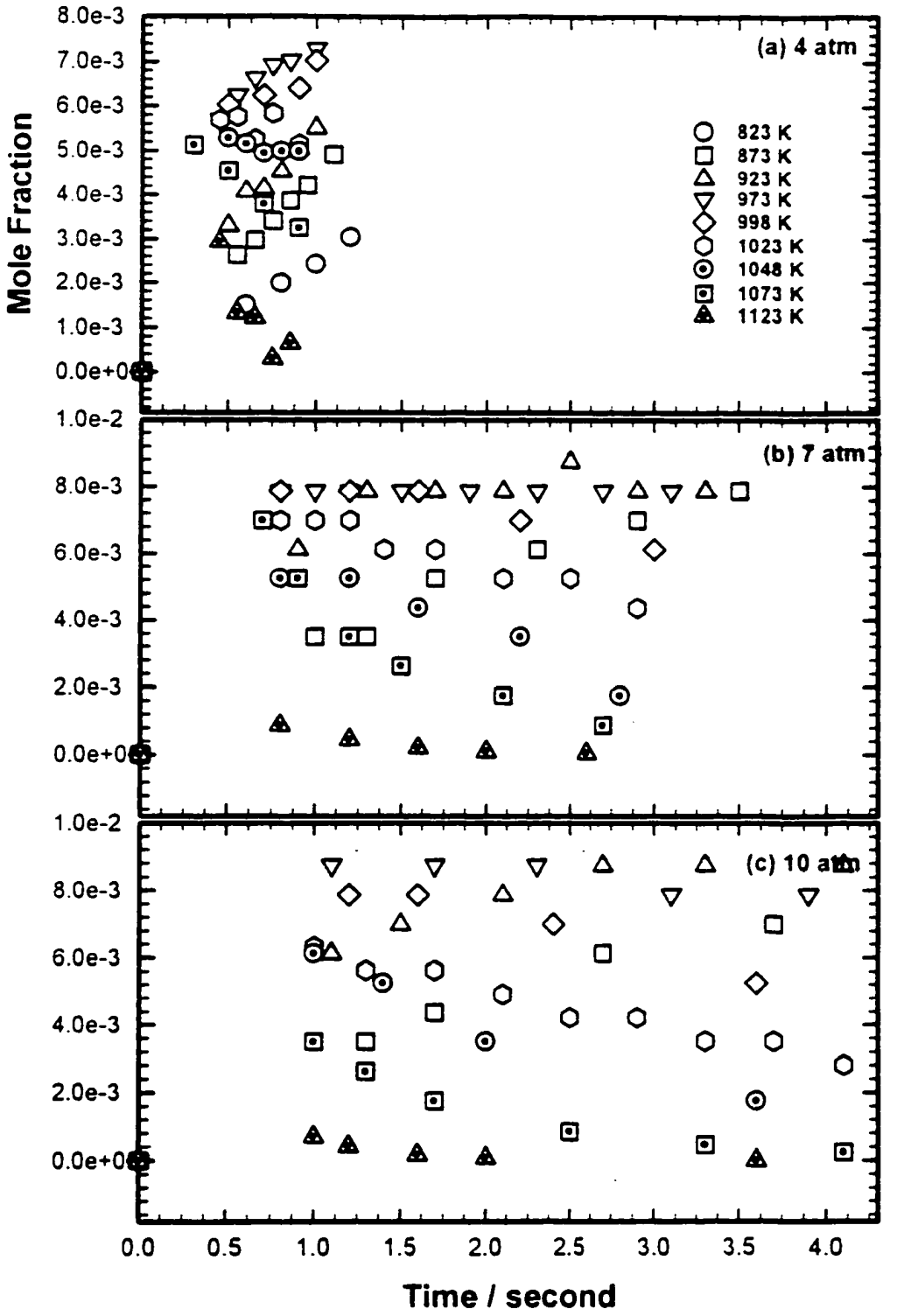


Figure IIC. 93 Experimental result of 0.5% MTBE pyrolysis: temperature and pressure dependence of $C_2C=C$

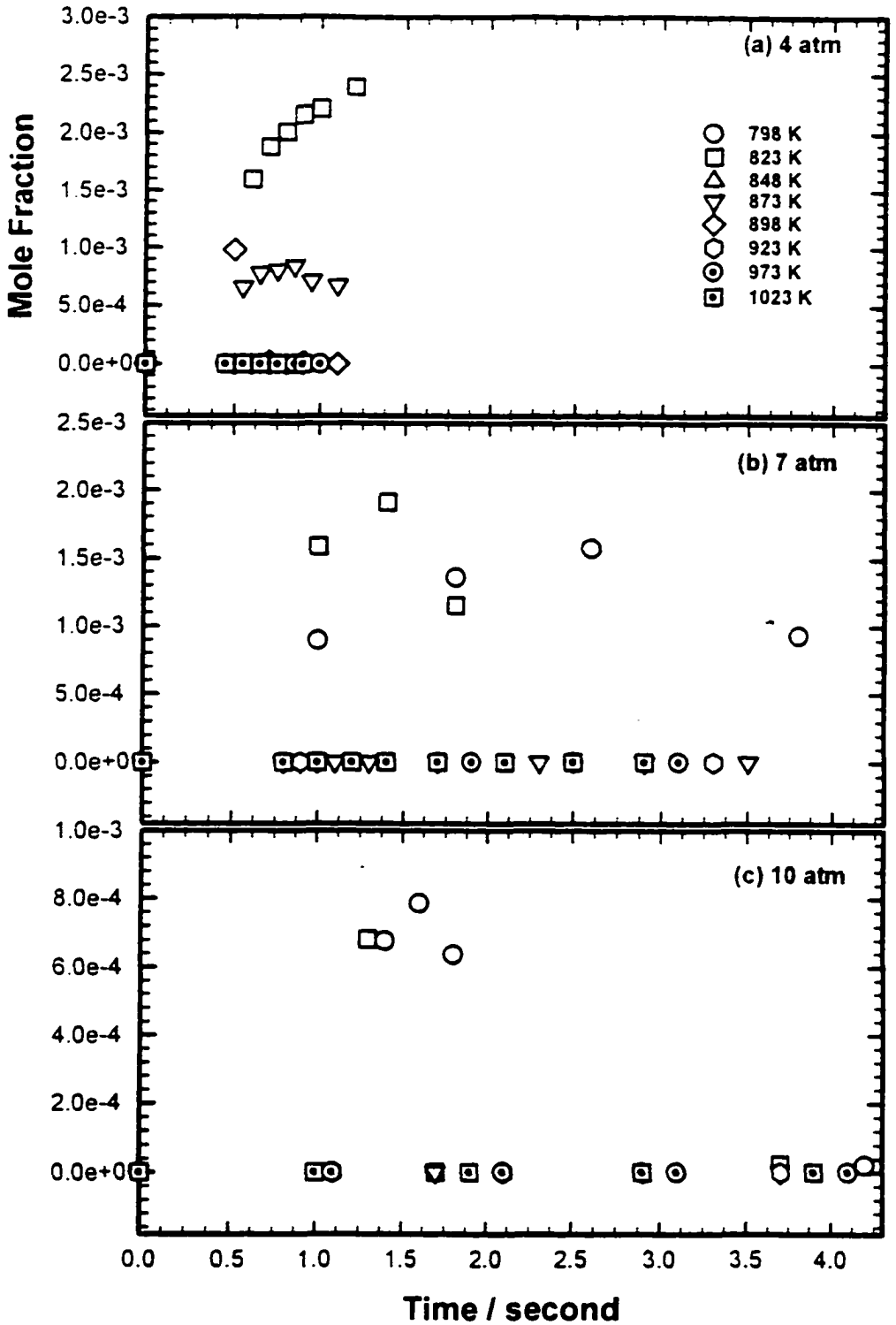


Figure IIC. 94 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CH_3OH at $\varphi = 0.75$

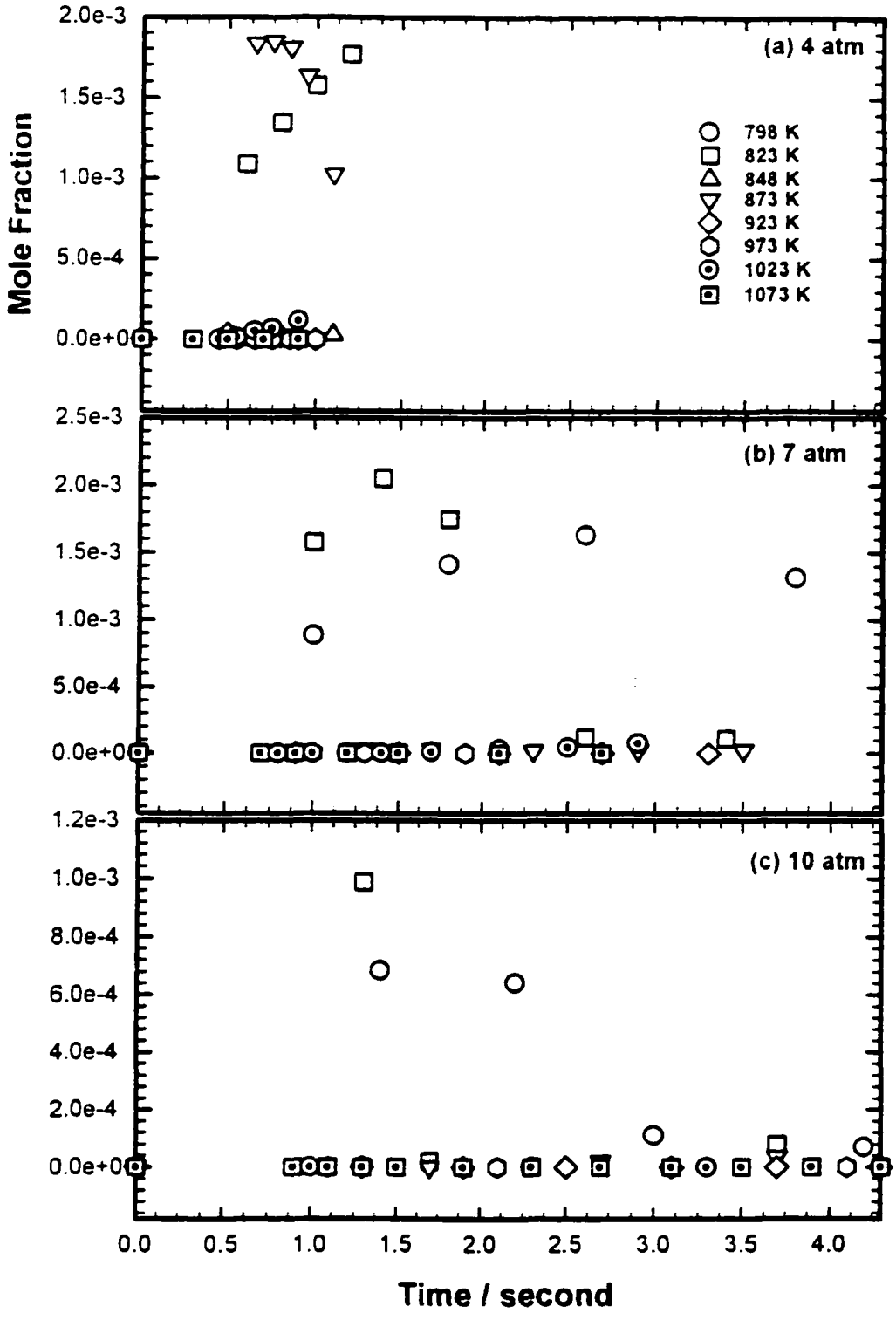


Figure IIC. 95 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CH_3OH at $\varphi = 1.00$

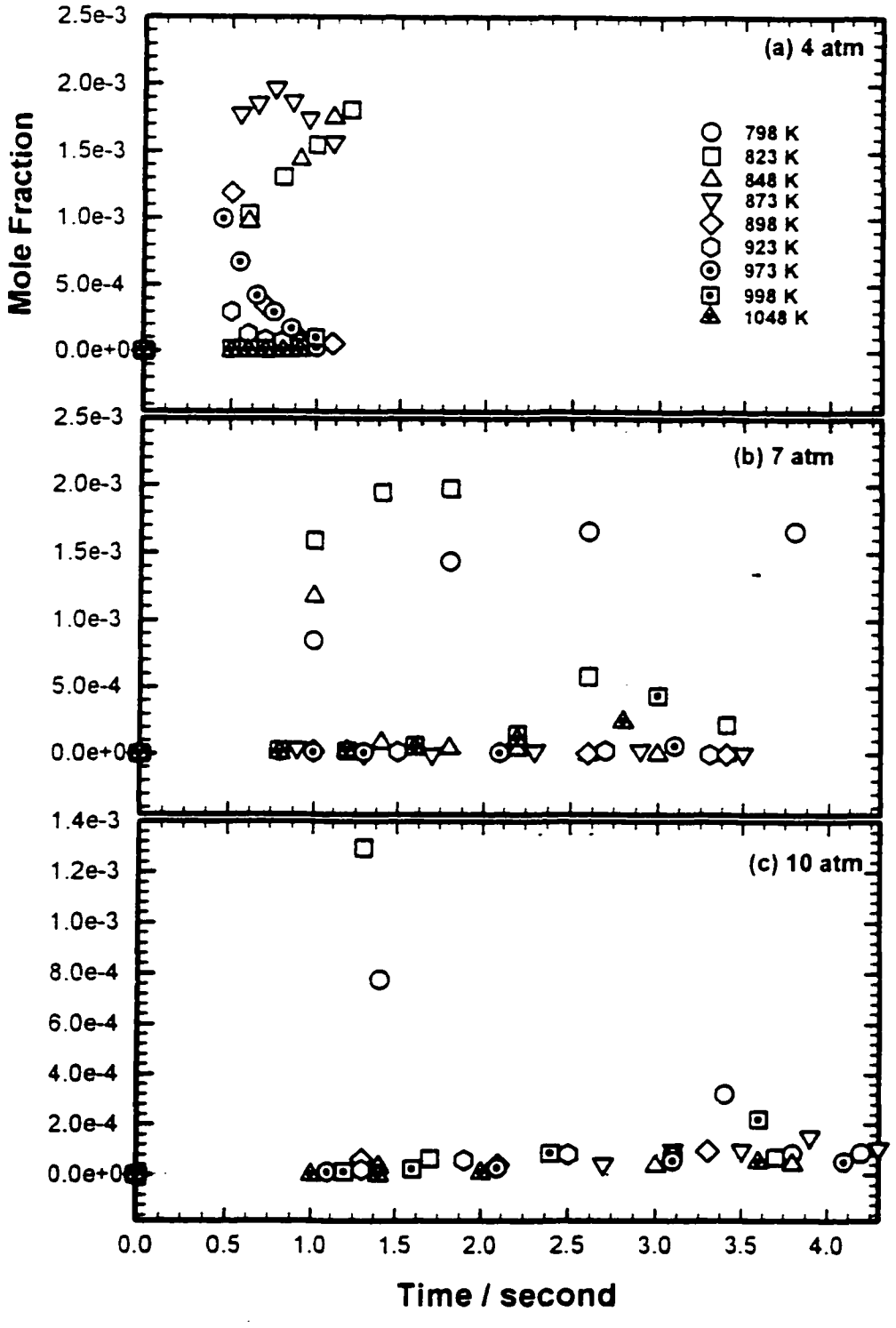


Figure IIC. 96 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CH_3OH at $\varphi = 1.50$

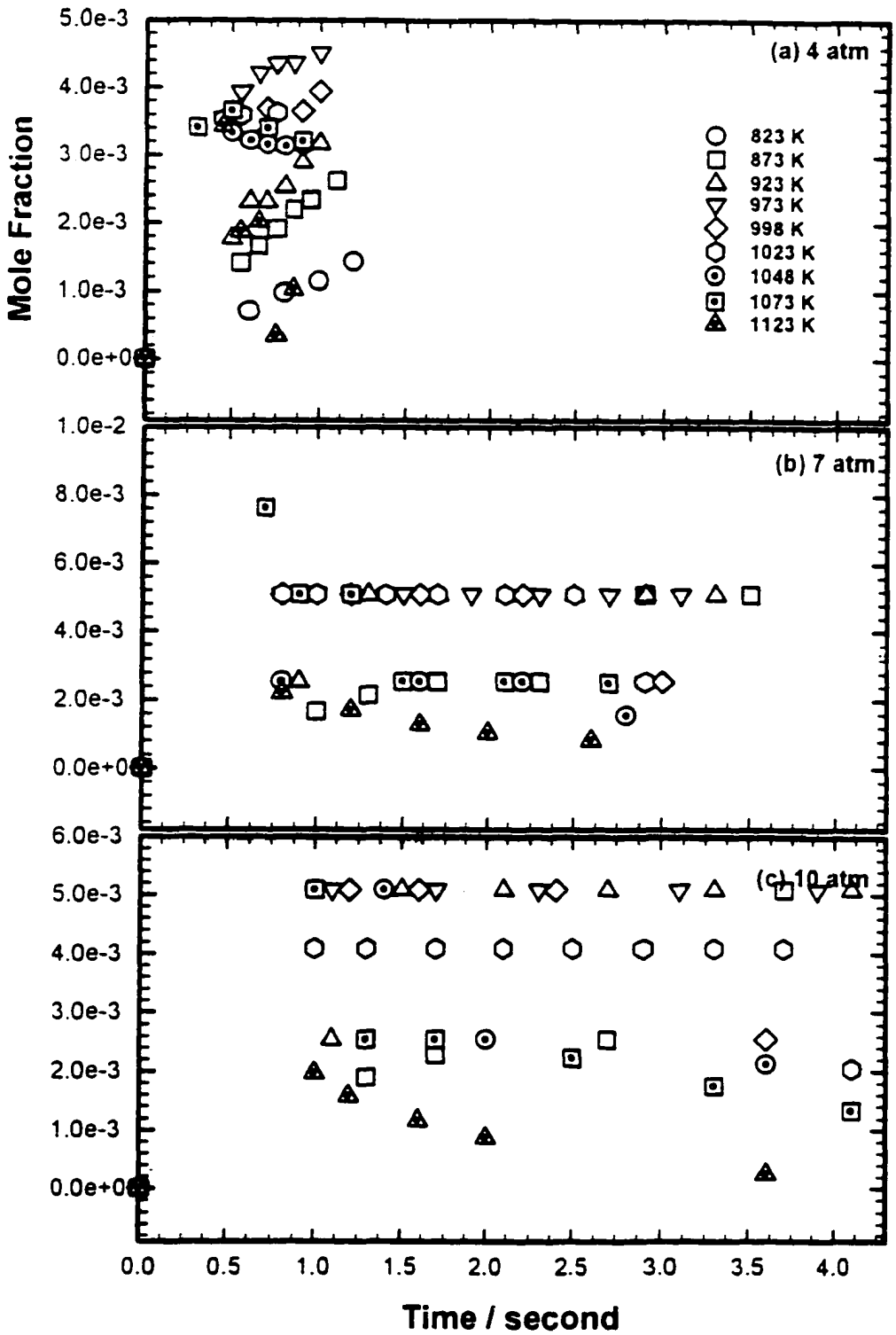


Figure IIC. 97 Experimental result of 0.5% MTBE pyrolysis: temperature and pressure dependence of CH_3OH

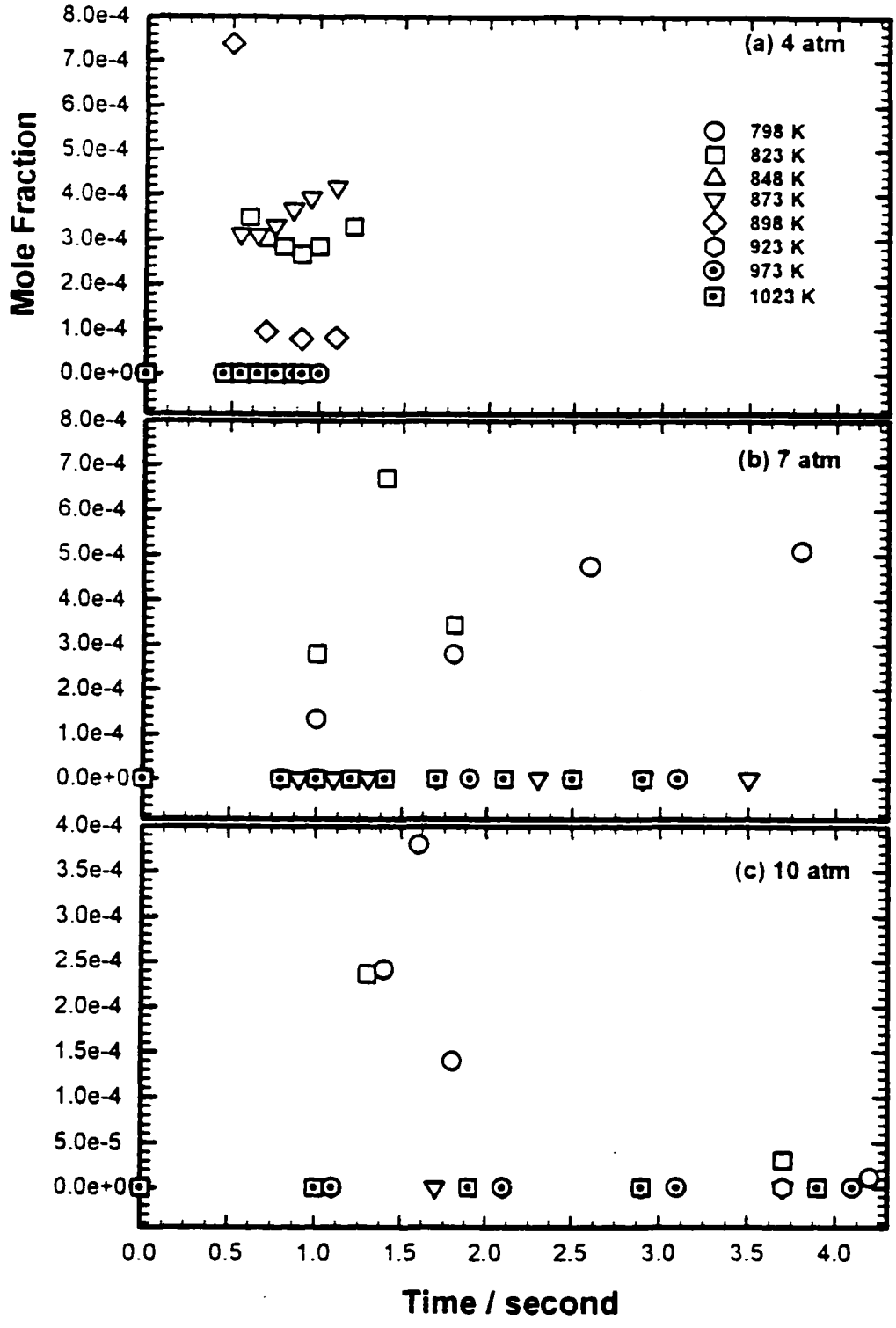


Figure IIC. 98 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CH_2O at $\varphi = 0.75$

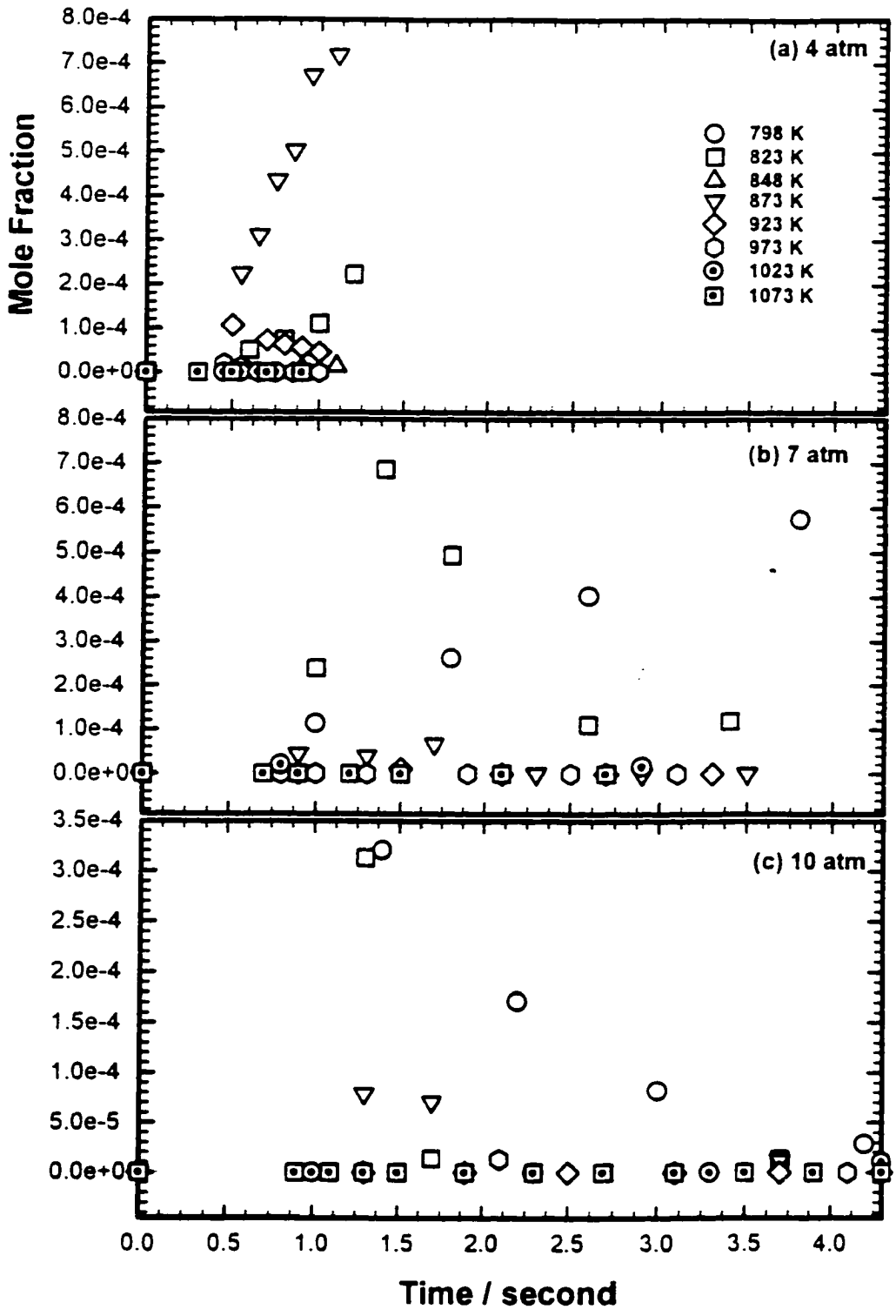


Figure IIC. 99 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CH_2O at φ = 1.00

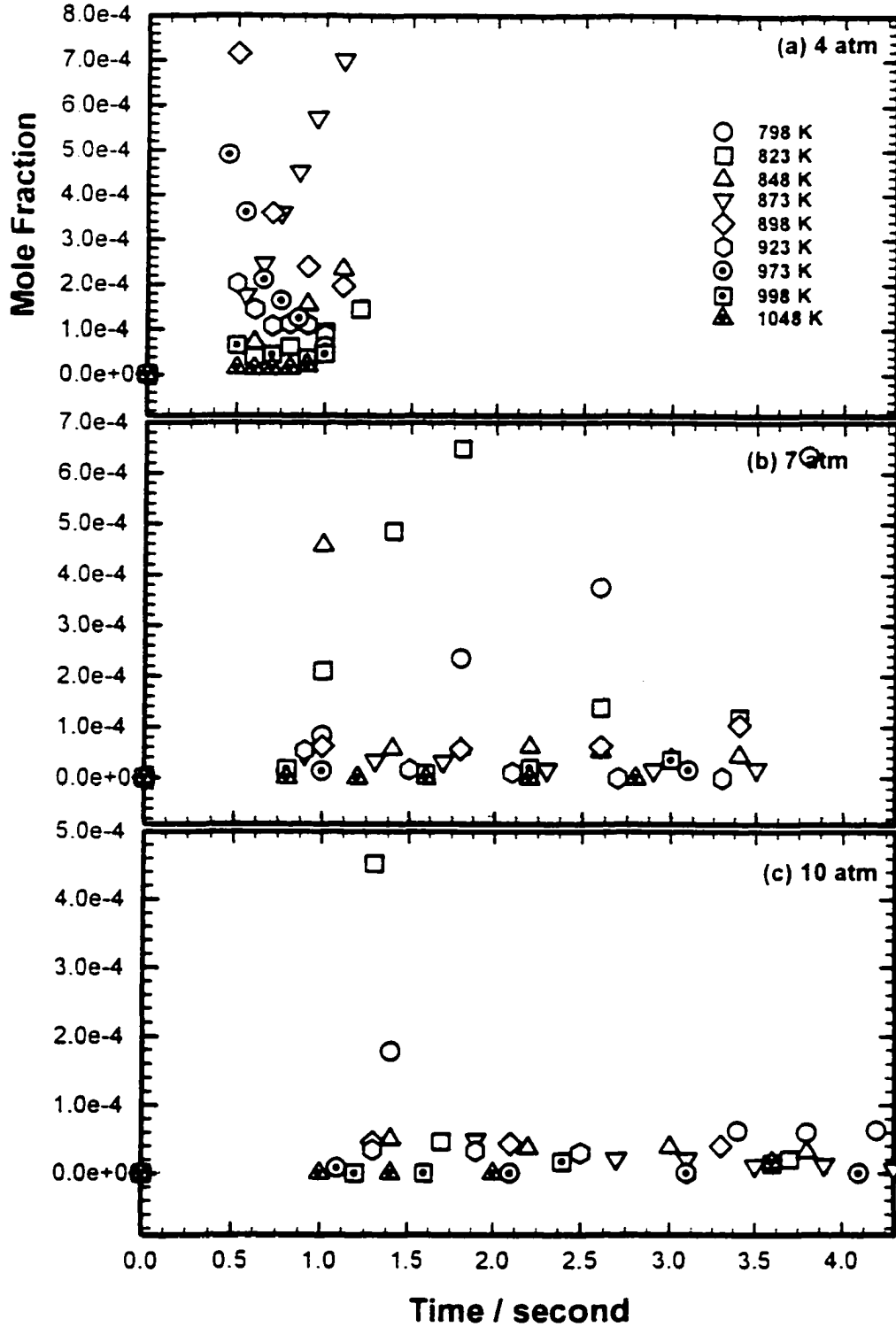


Figure IIC. 100 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CH_2O at $\varphi = 1.50$

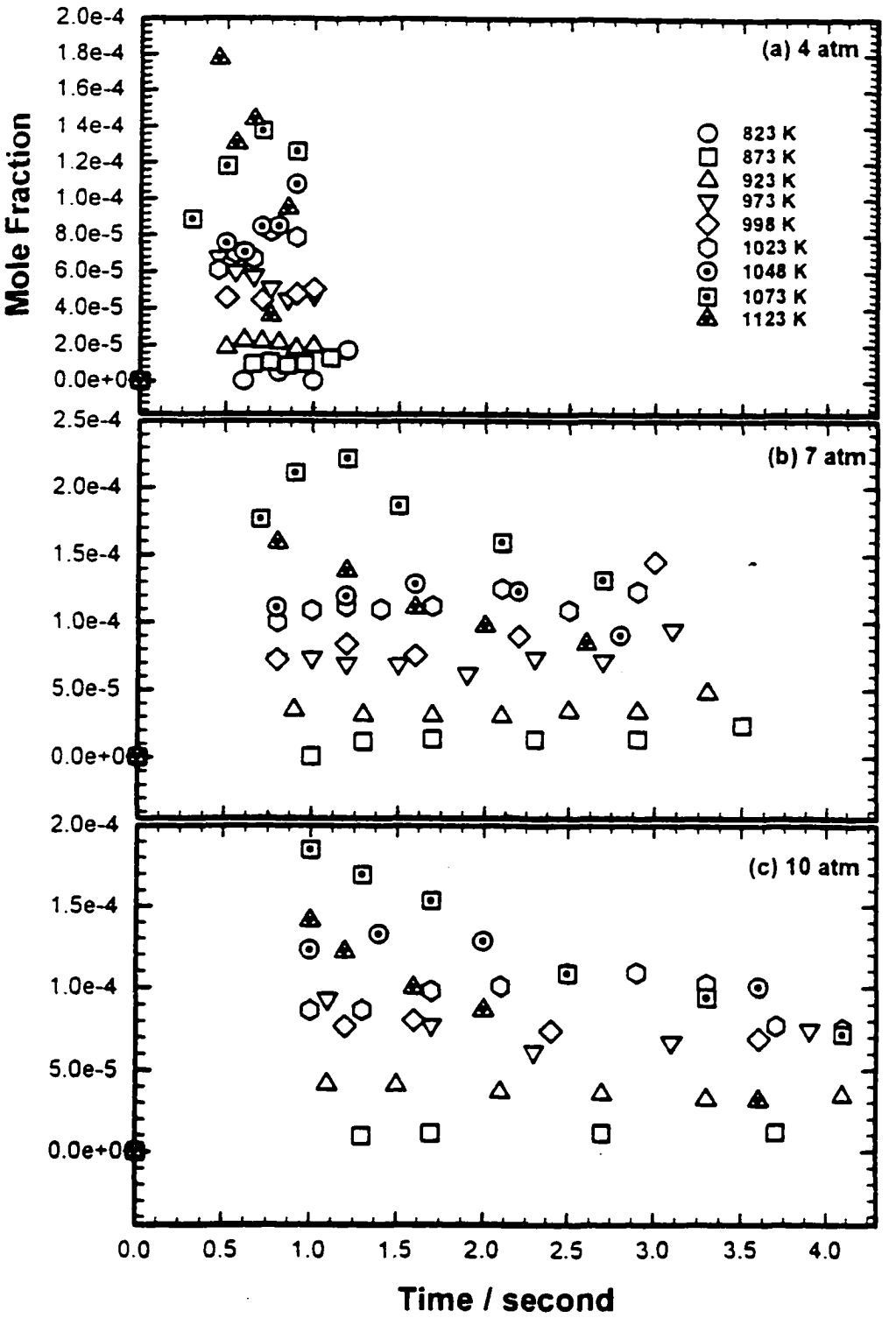


Figure IIC. 101 Experimental result of 0.5% MTBE pyrolysis: temperature and pressure dependence of CH_2O

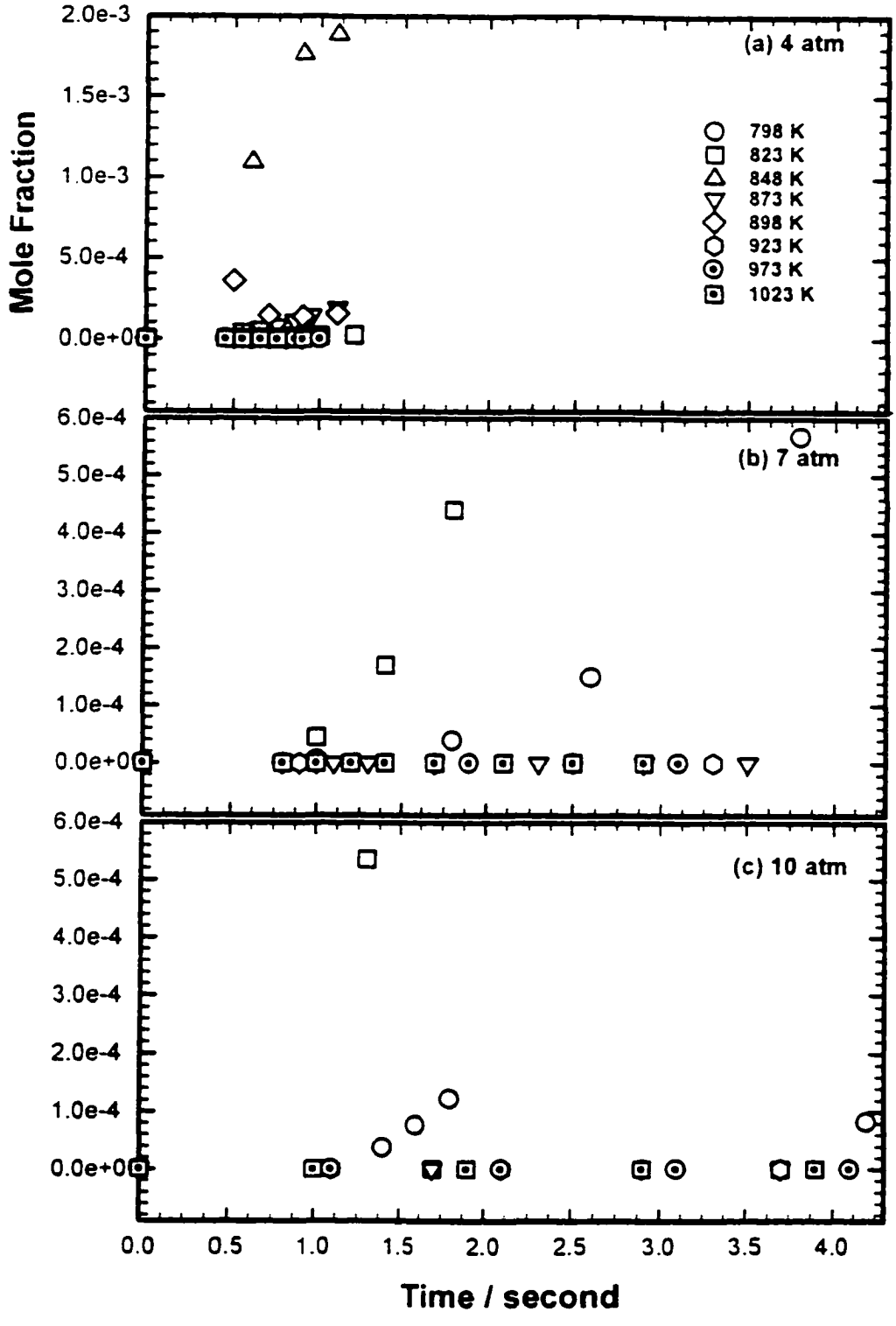


Figure IIC. 102 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of $C_2C{=}O$ at $\varphi = 0.75$

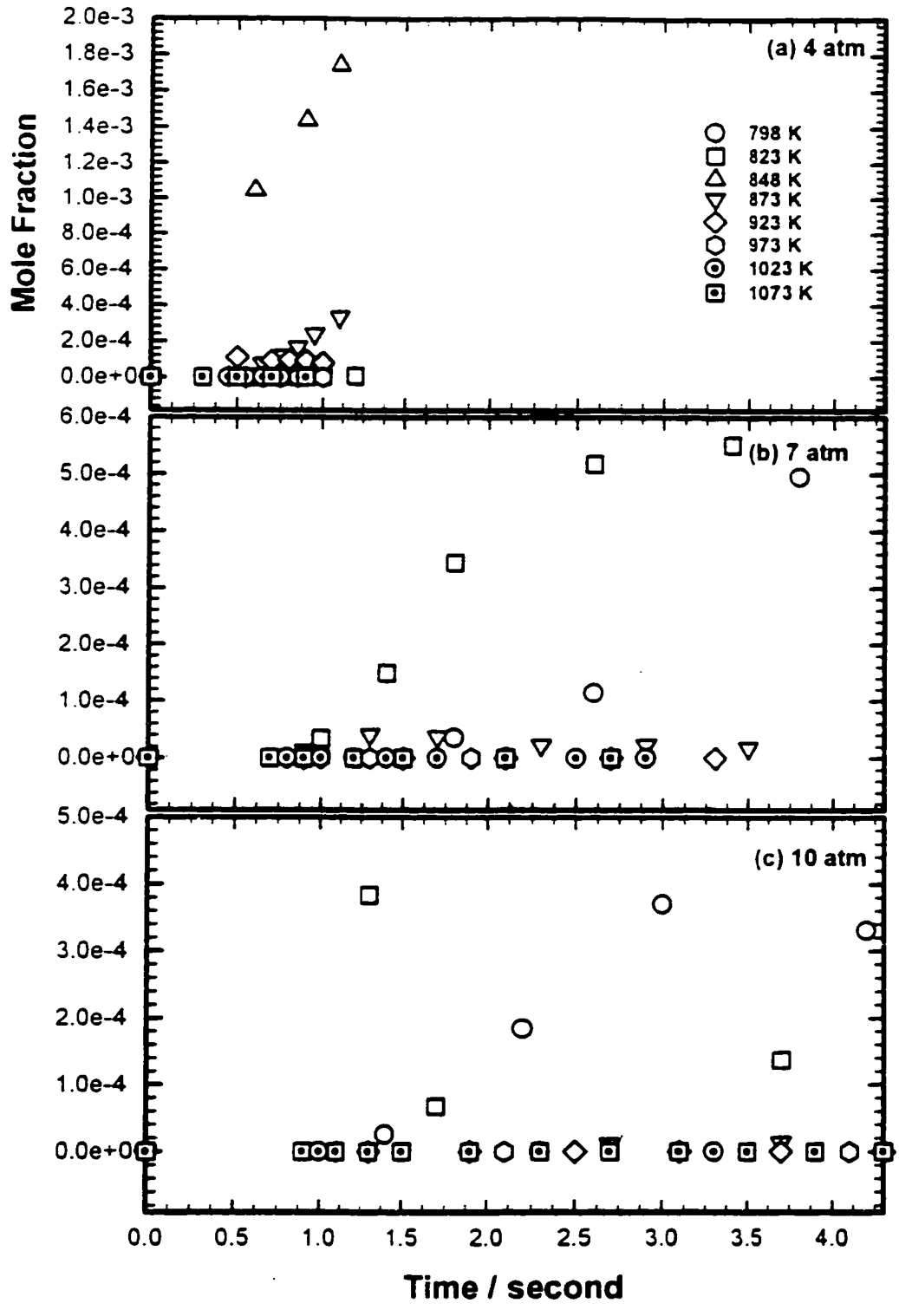


Figure IIC. 103 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of $C_2C=O$ at φ = 1.00

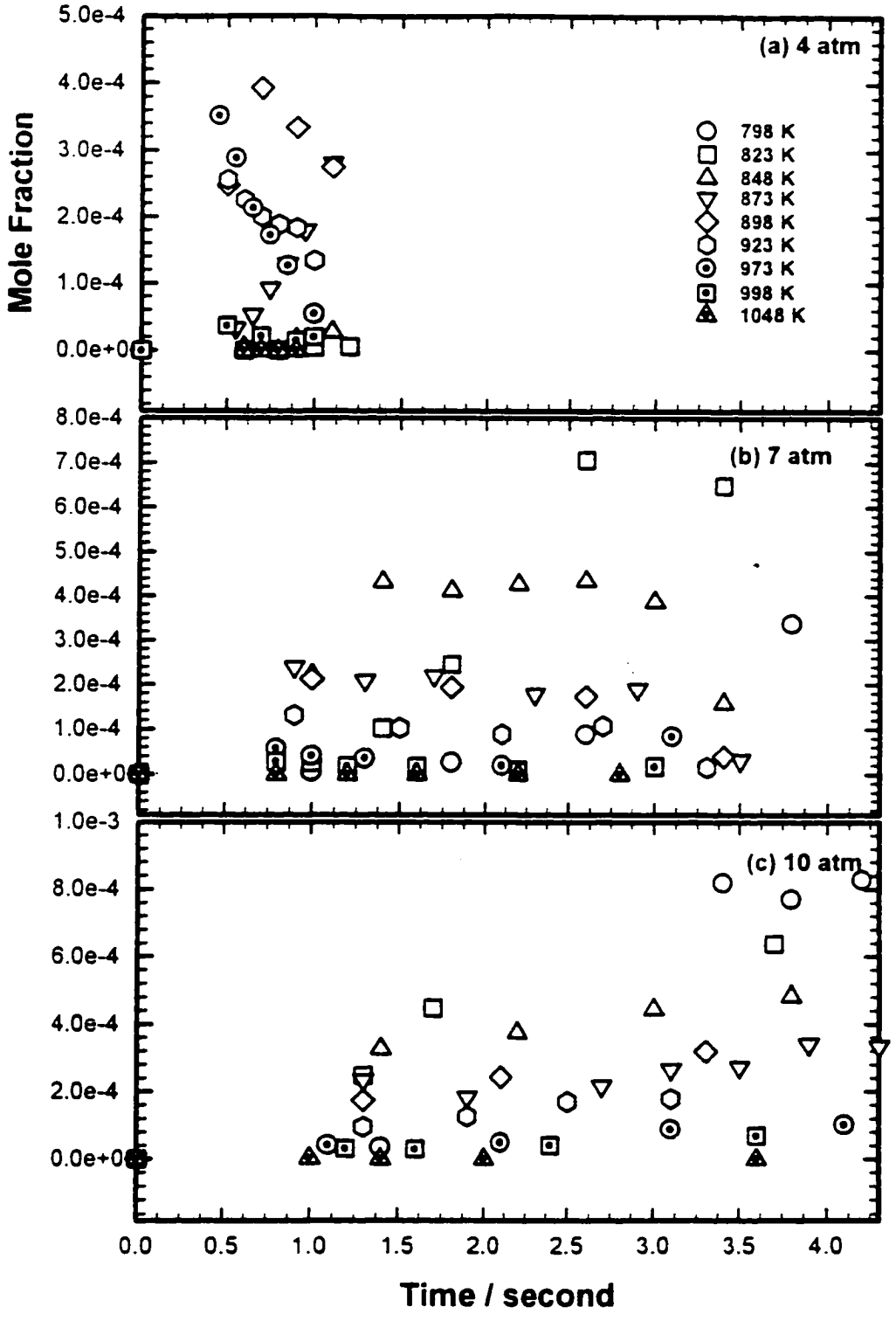


Figure IIC. 104 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of $C_2C{=}O$ at $\varphi = 1.50$

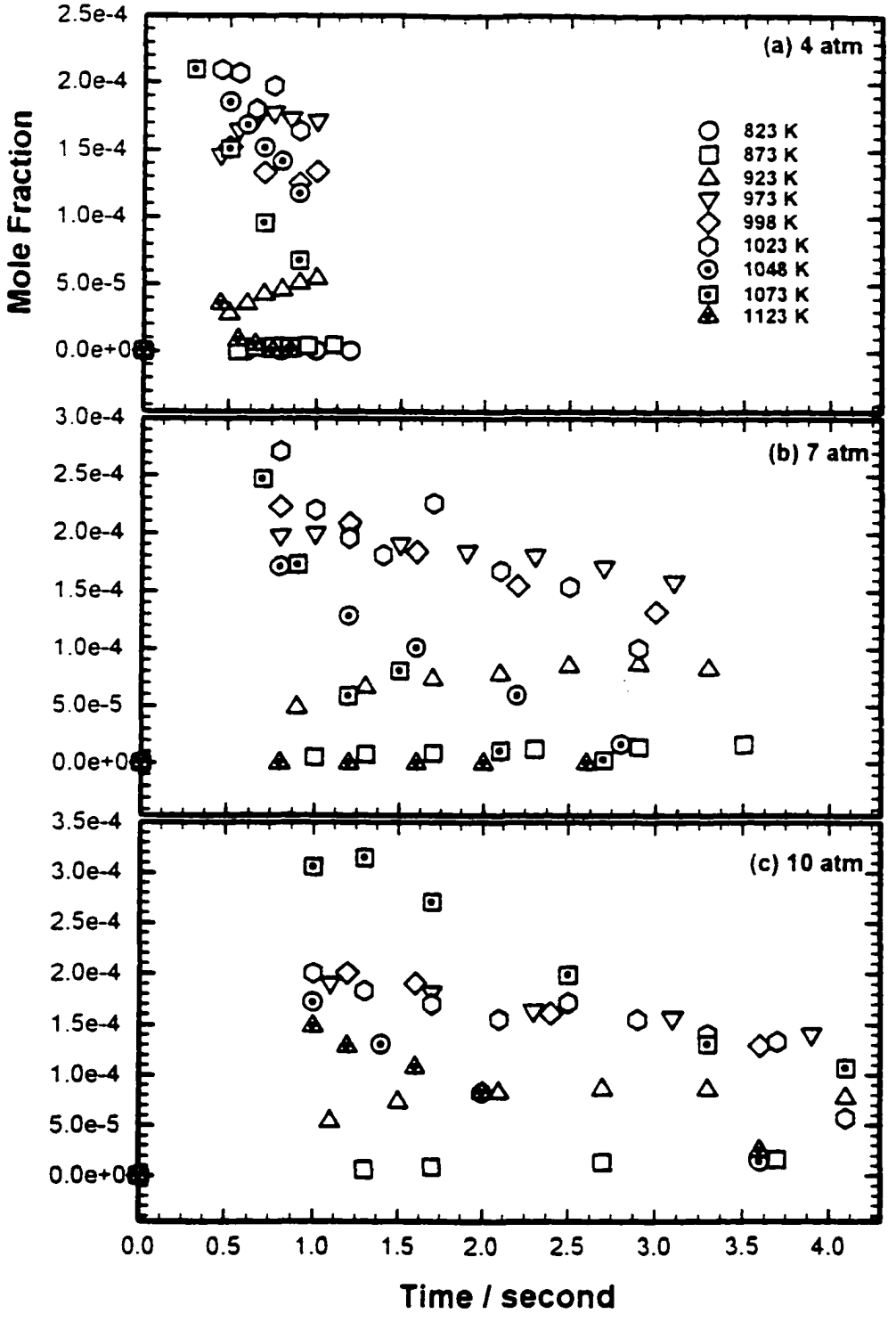


Figure IIC. 105 Experimental result of 0.5% MTBE pyrolysis: temperature and pressure dependence of $C_2C=O$

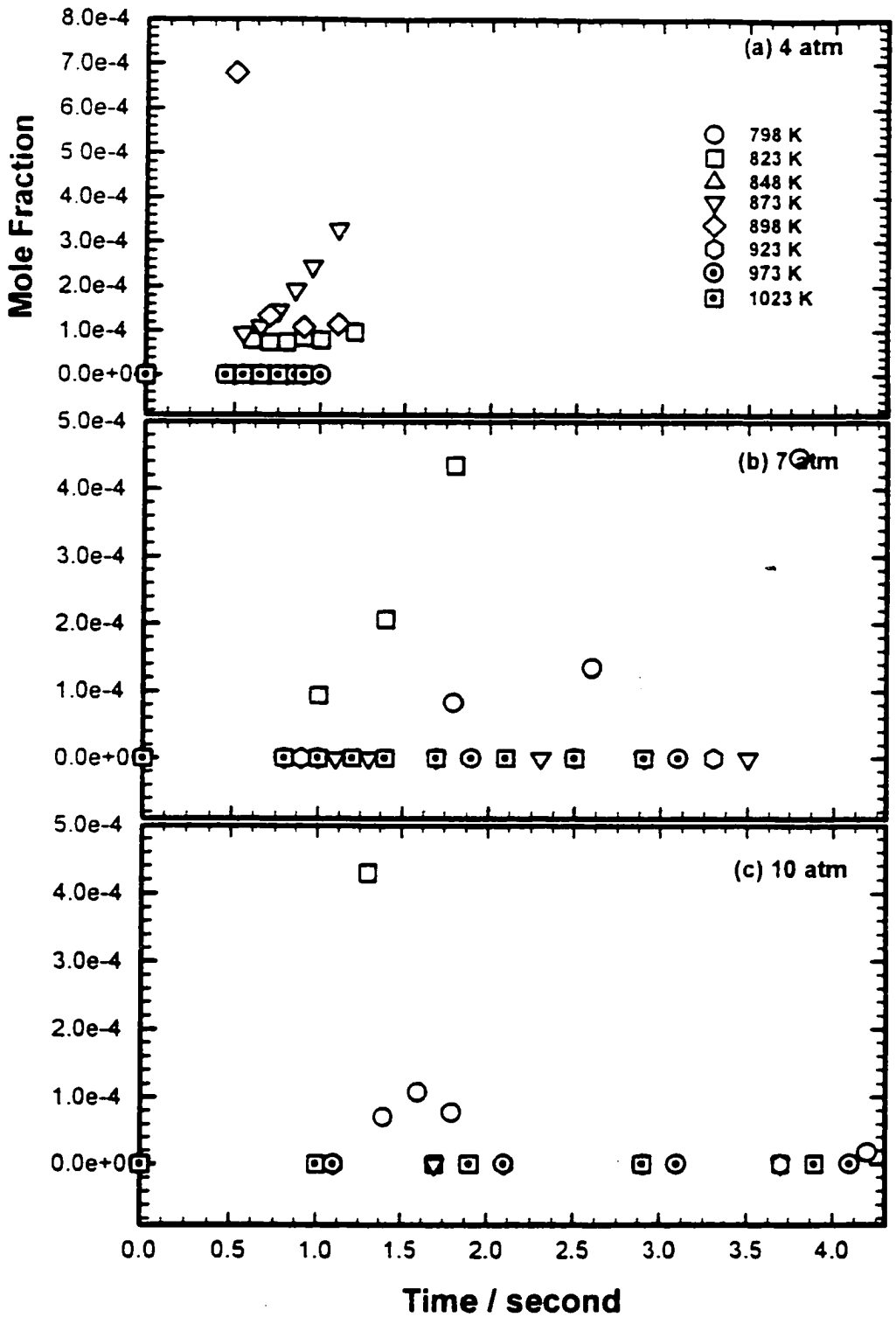


Figure IIC. 106 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of C_3H_6 at $\varphi = 0.75$

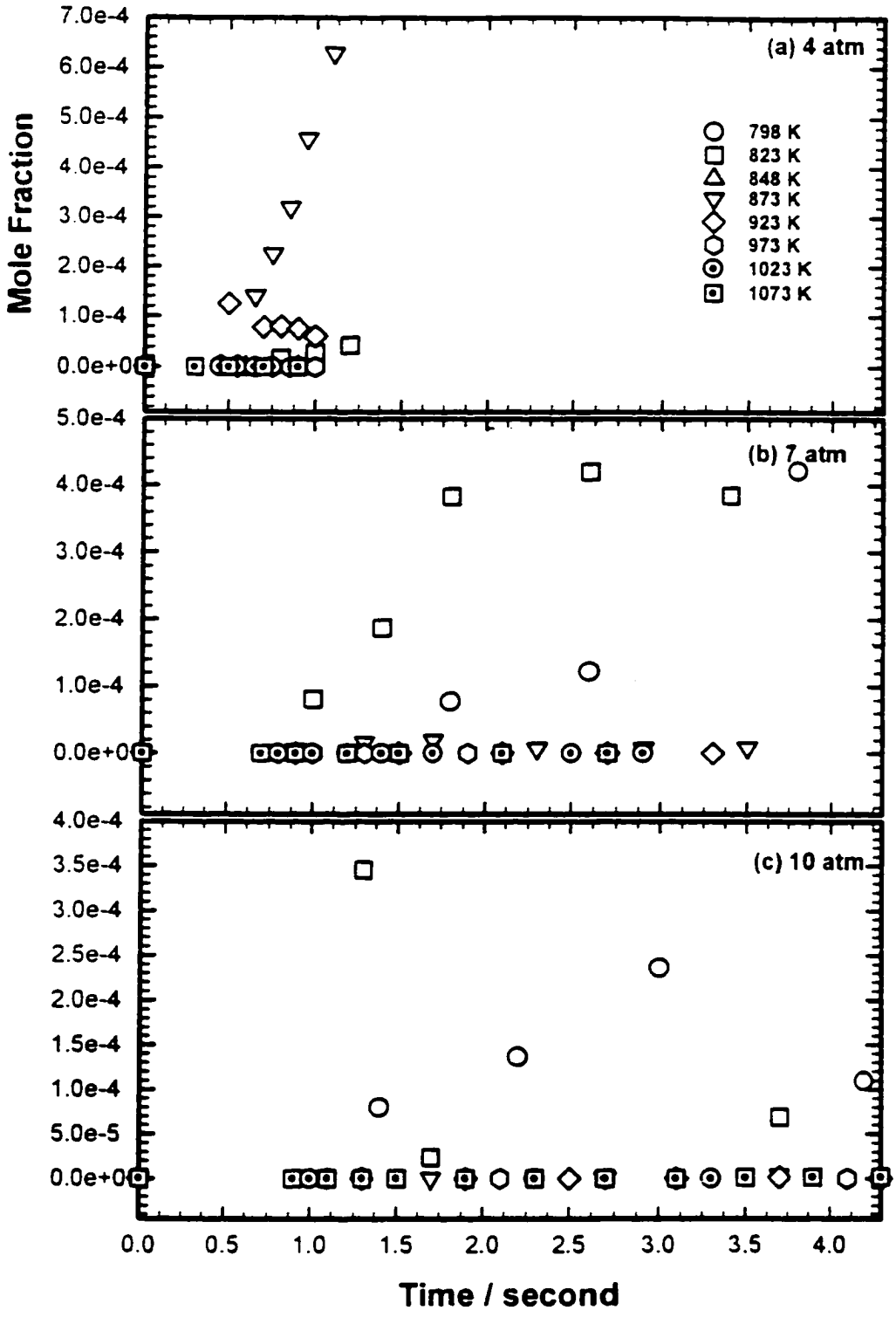


Figure IIC. 107 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of C_3H_6 at $\varphi = 1.00$

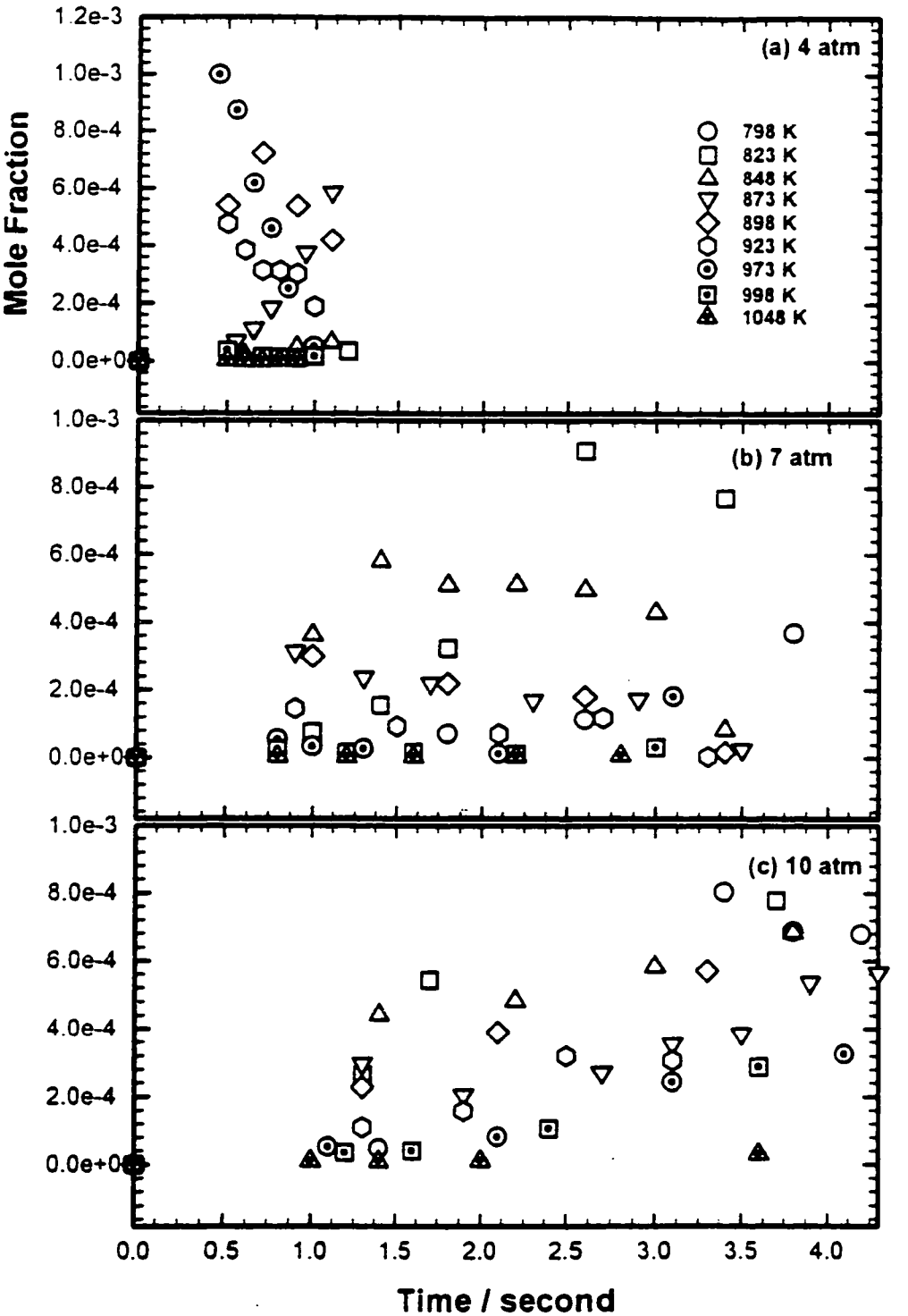


Figure IIC. 108 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of C_3H_6 at φ = 1.50

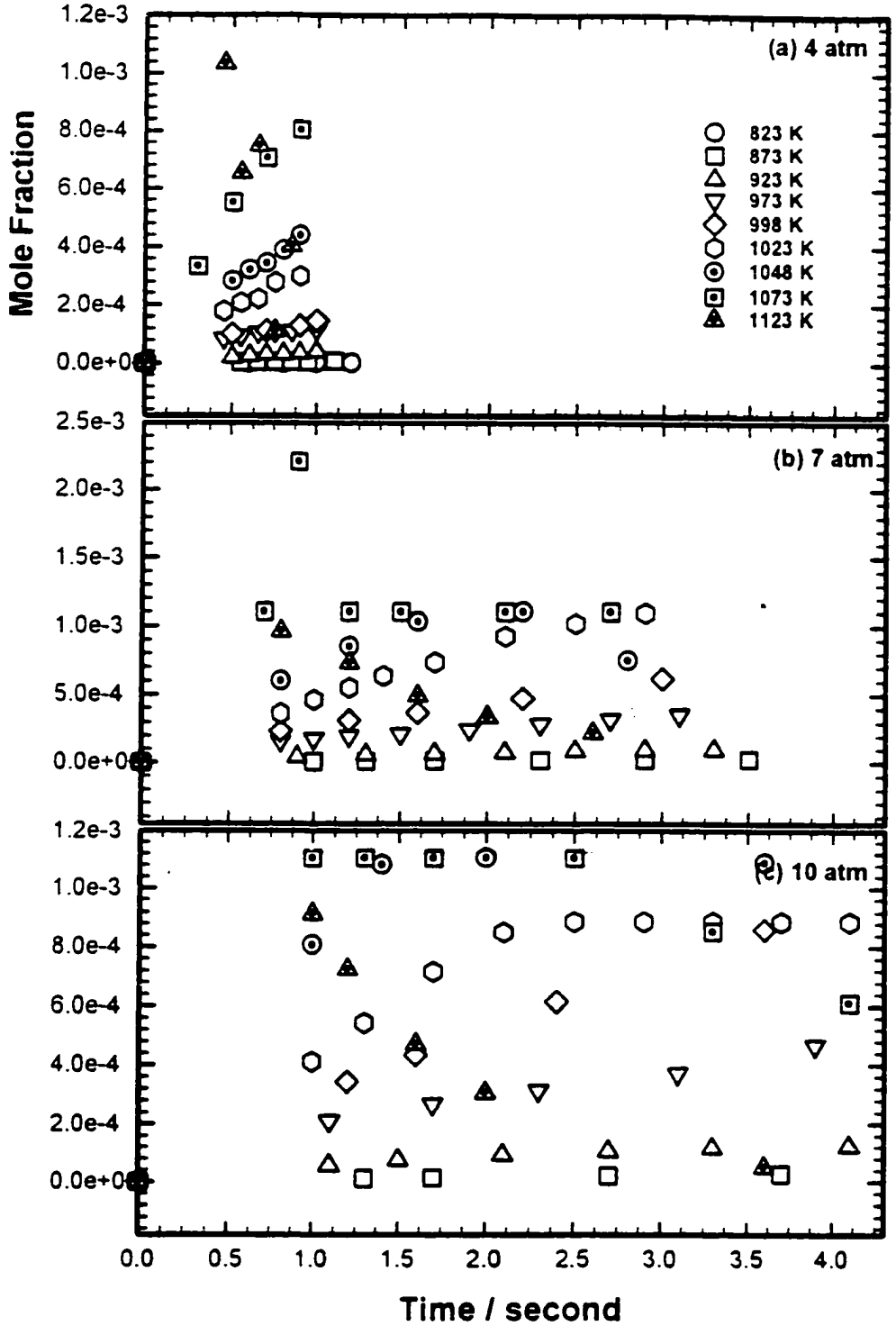


Figure IIC. 109 Experimental result of 0.5% MTBE pyrolysis: temperature and pressure dependence of C_3H_6

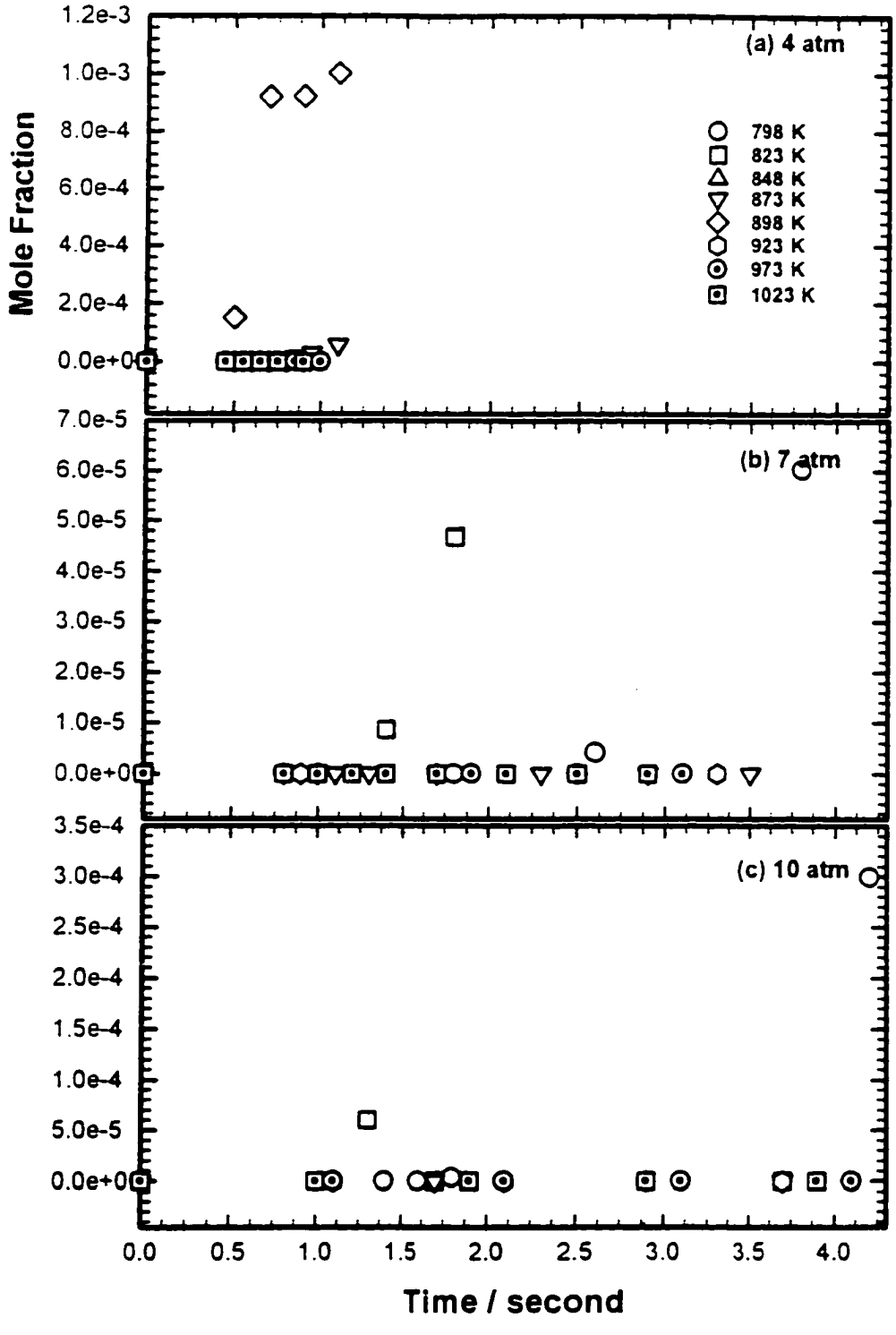


Figure IIC. 110 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of C_2H_4 at $\varphi = 0.75$

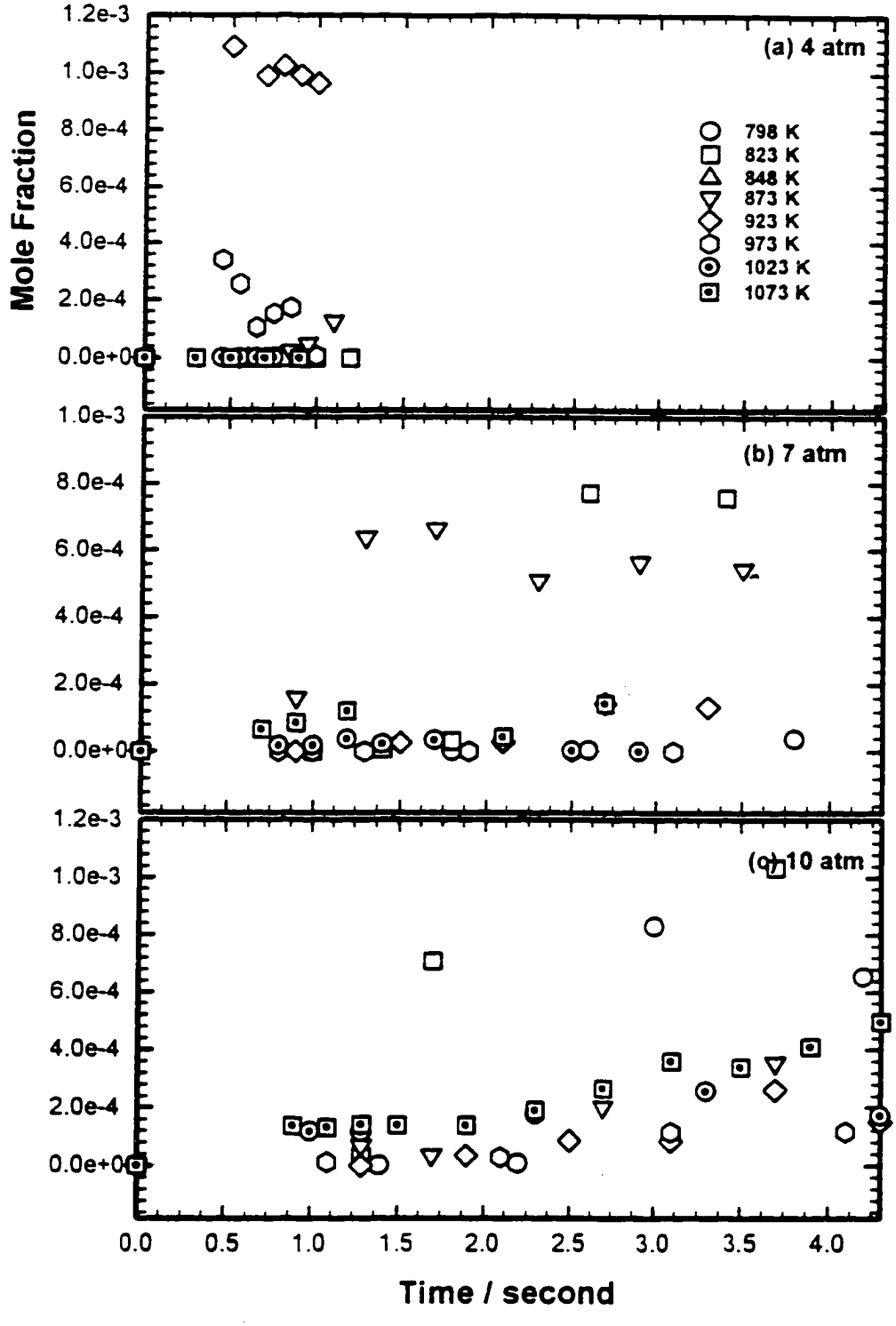


Figure IIC. 111 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of C_2H_4 at φ = 1.00

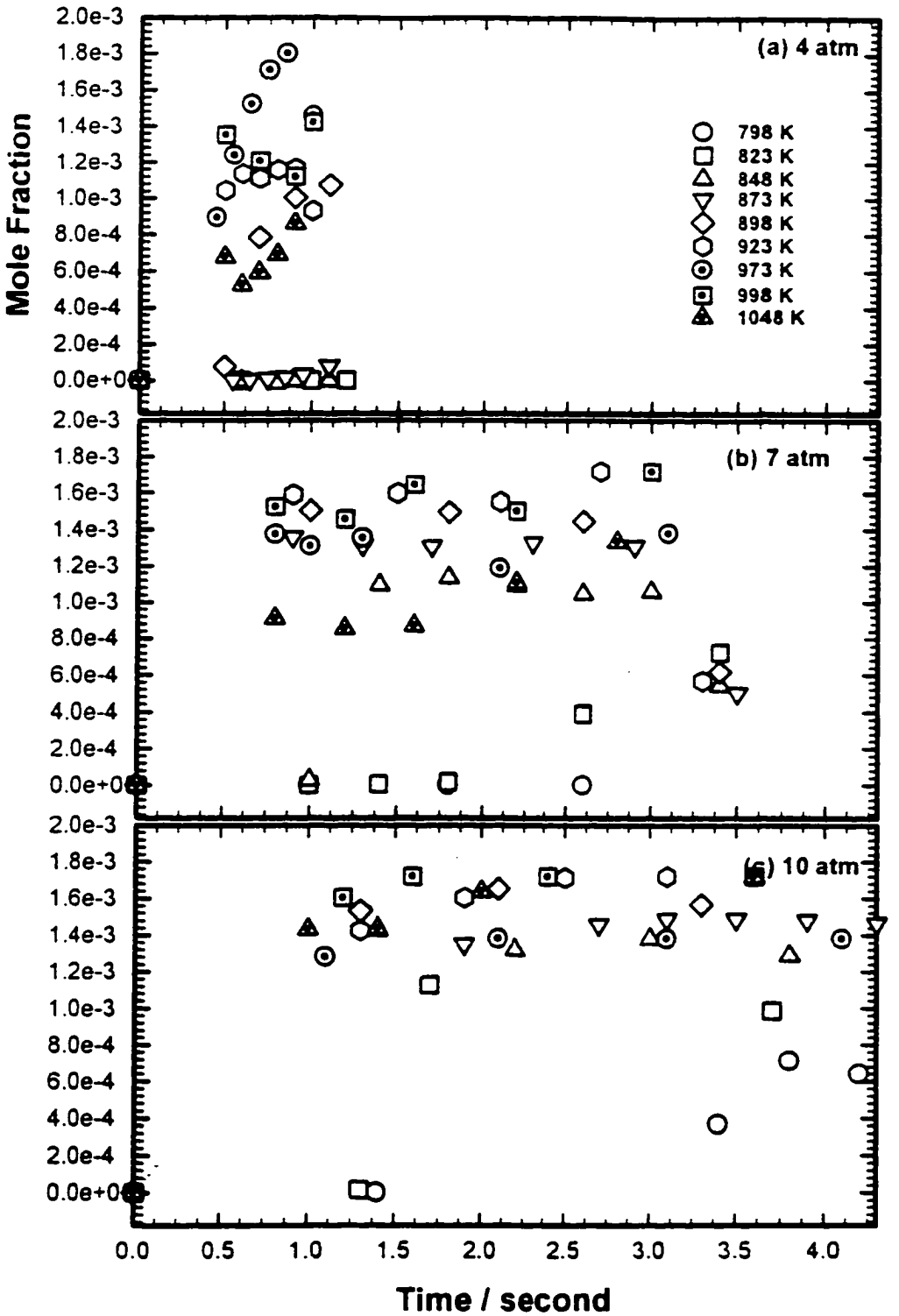


Figure IIC. 112 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of C_2H_4 at $\varphi = 1.50$

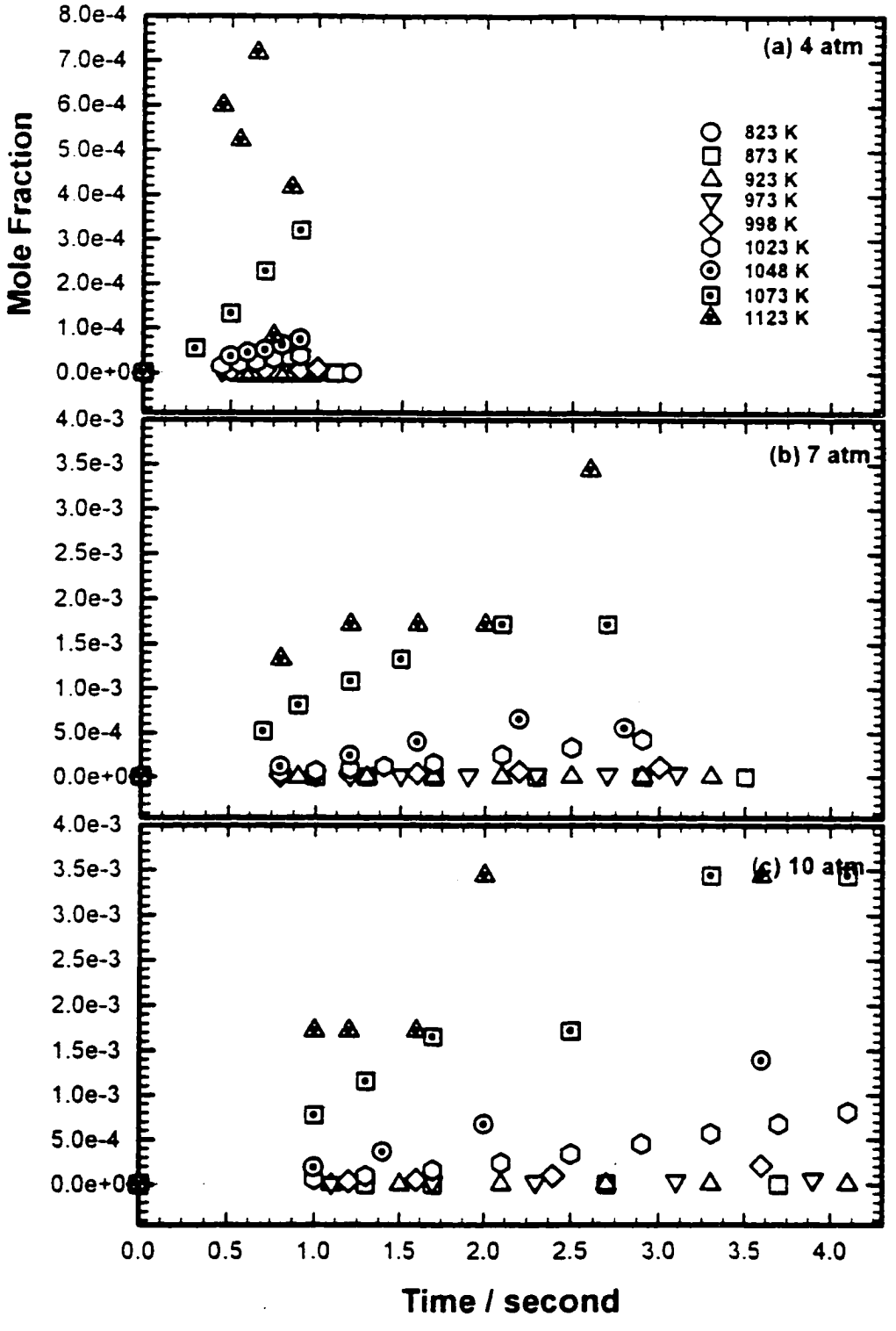


Figure IIC. 113 Experimental result of 0.5% MTBE pyrolysis: temperature and pressure dependence of C_2H_4

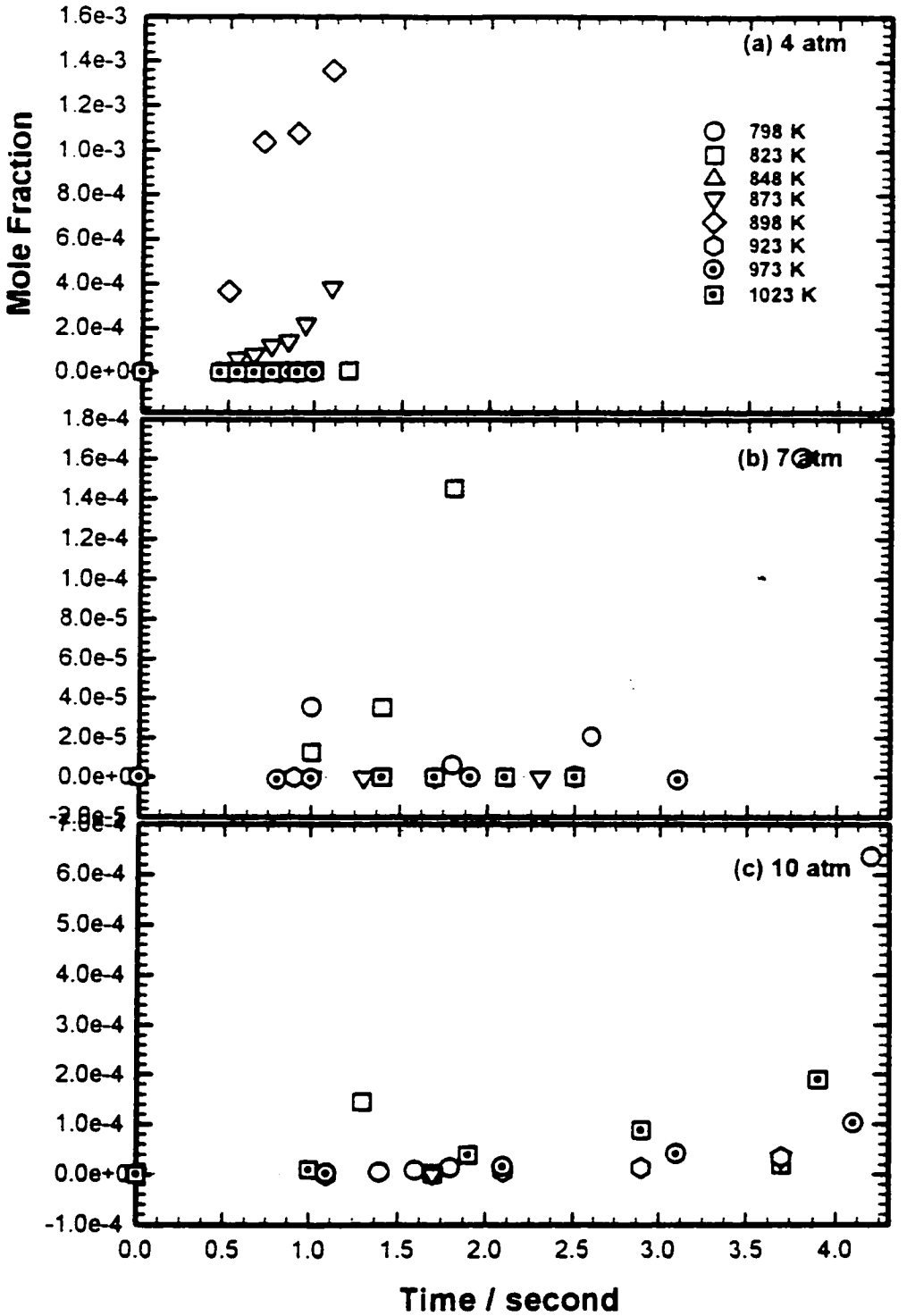


Figure IIC. 114 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CH_4 at $\varphi = 0.75$

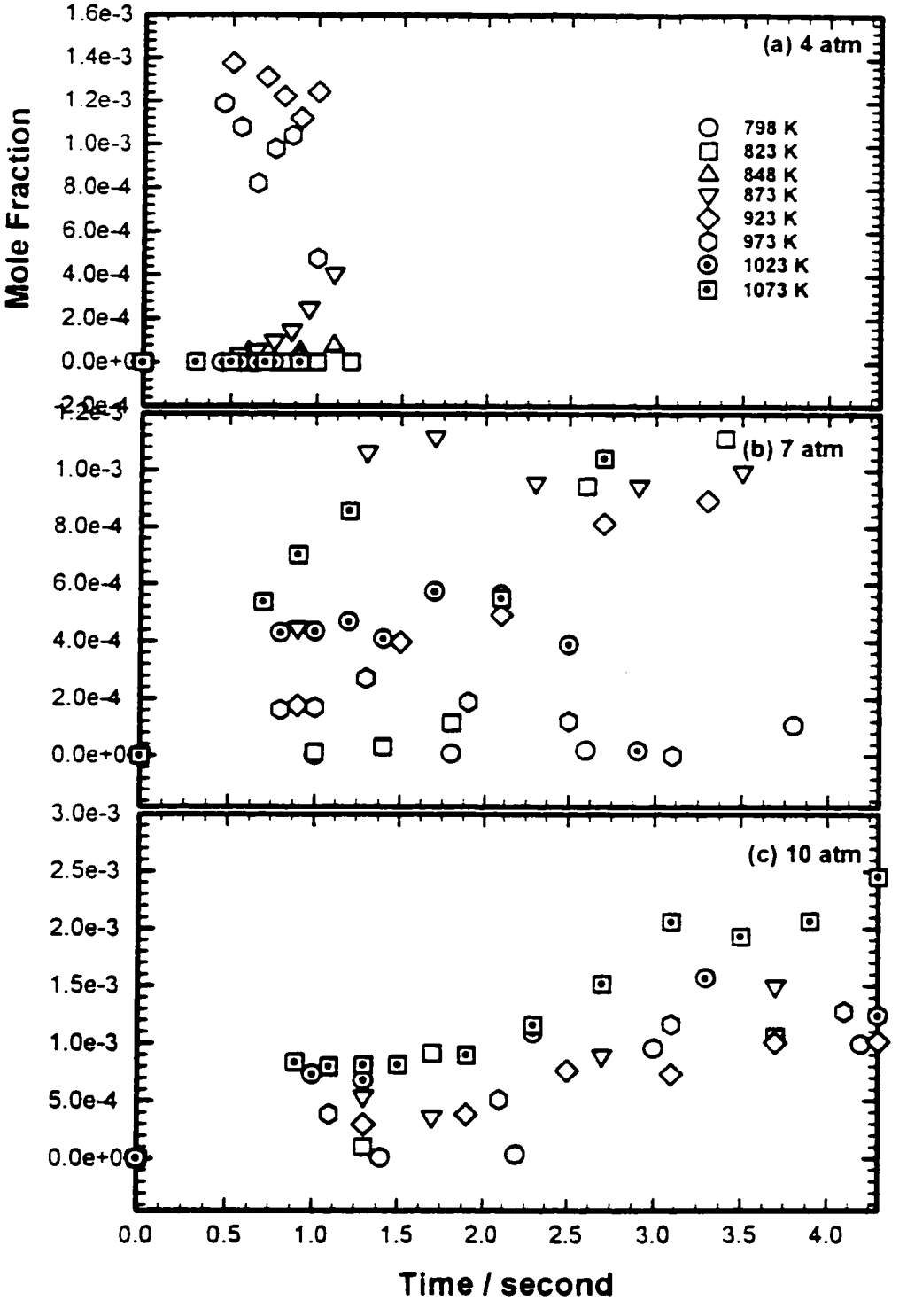


Figure IIC. 115 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CH_4 at φ = 1.00

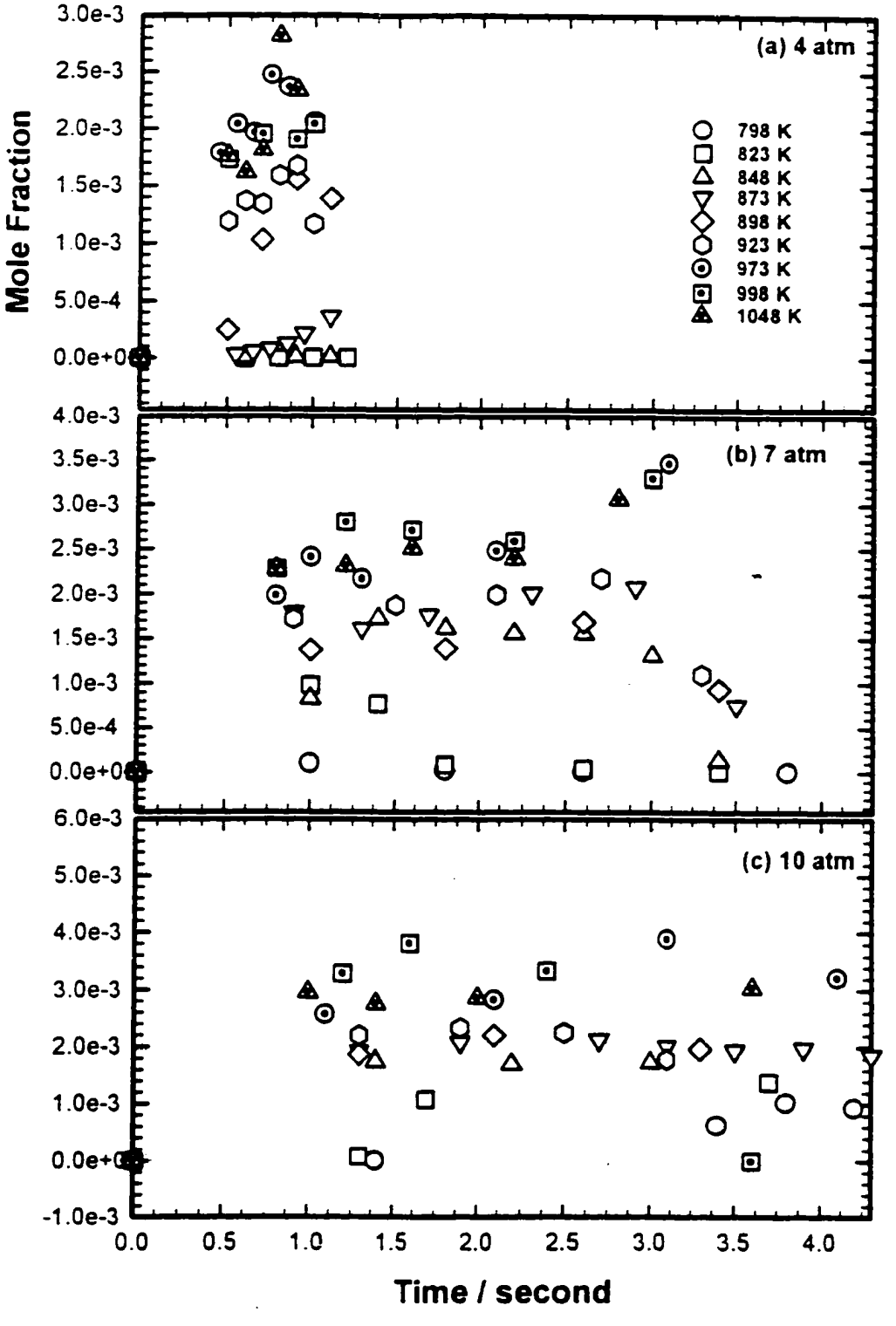


Figure IIC. 116 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CH_4 at $\varphi = 1.50$

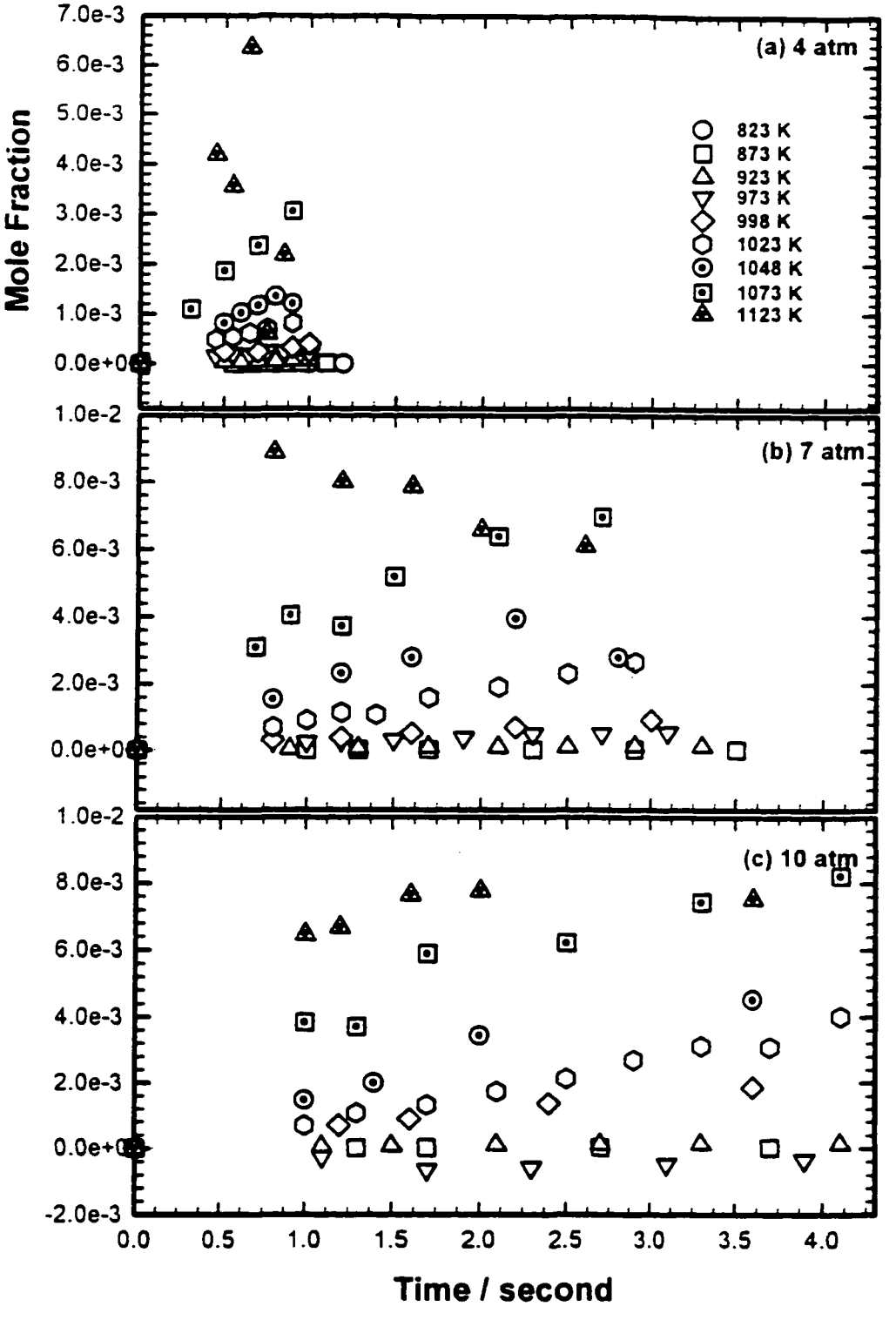


Figure IIC. 117 Experimental result of 0.5% MTBE pyrolysis: temperature and pressure dependence of CH_4

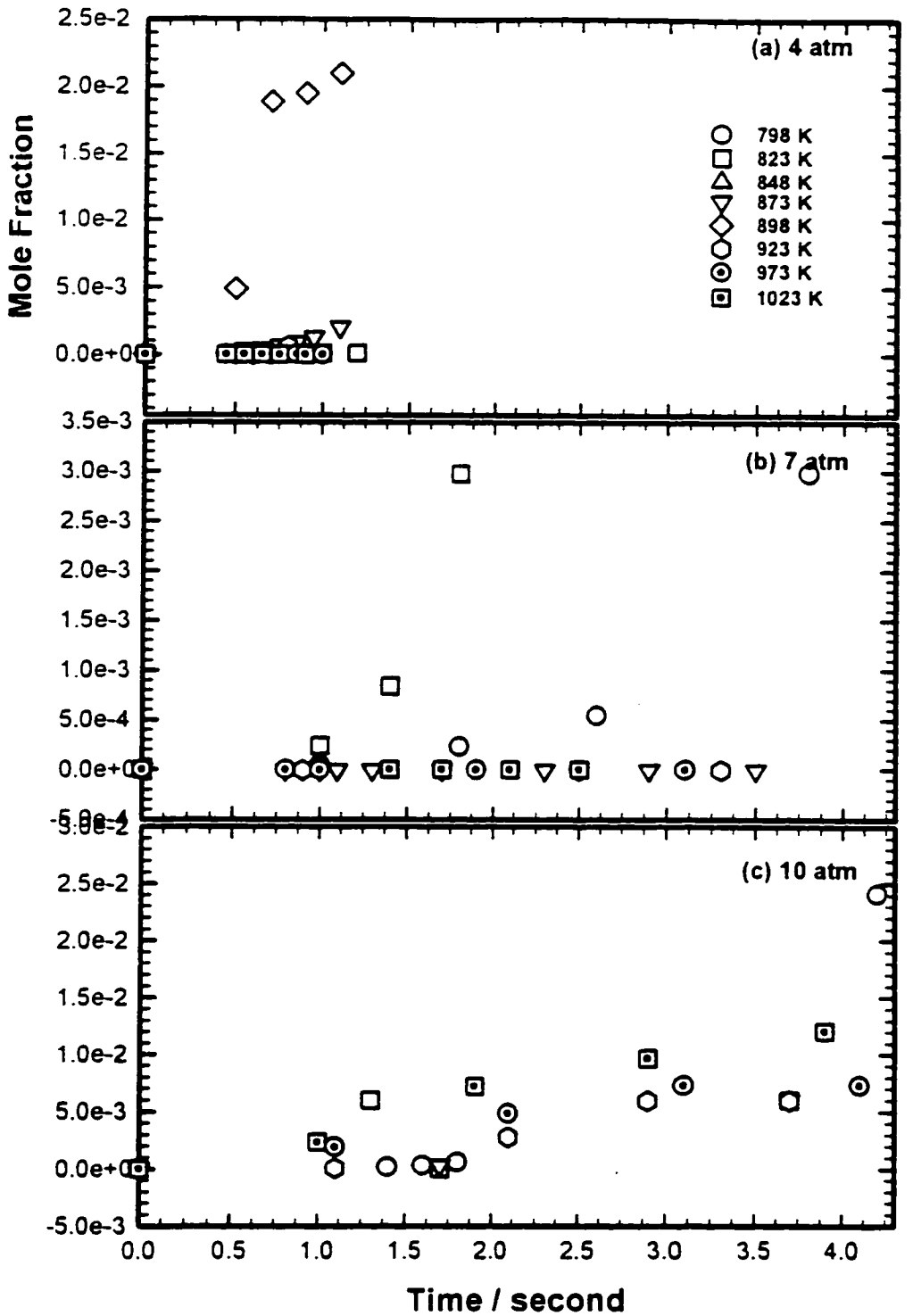


Figure IIC. 118 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CO at $\varphi = 0.75$

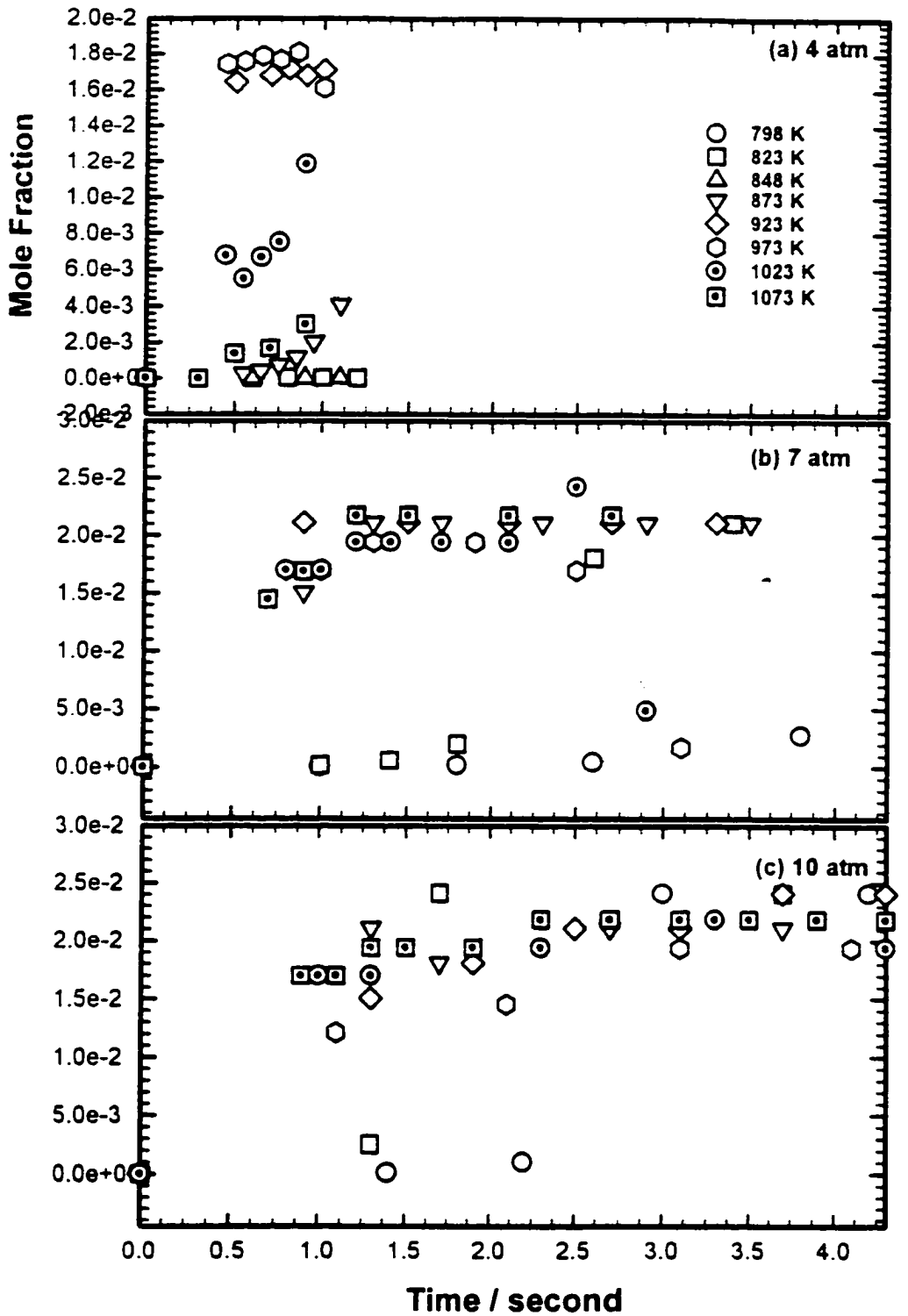


Figure IIC. 119 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CO at φ = 1.00

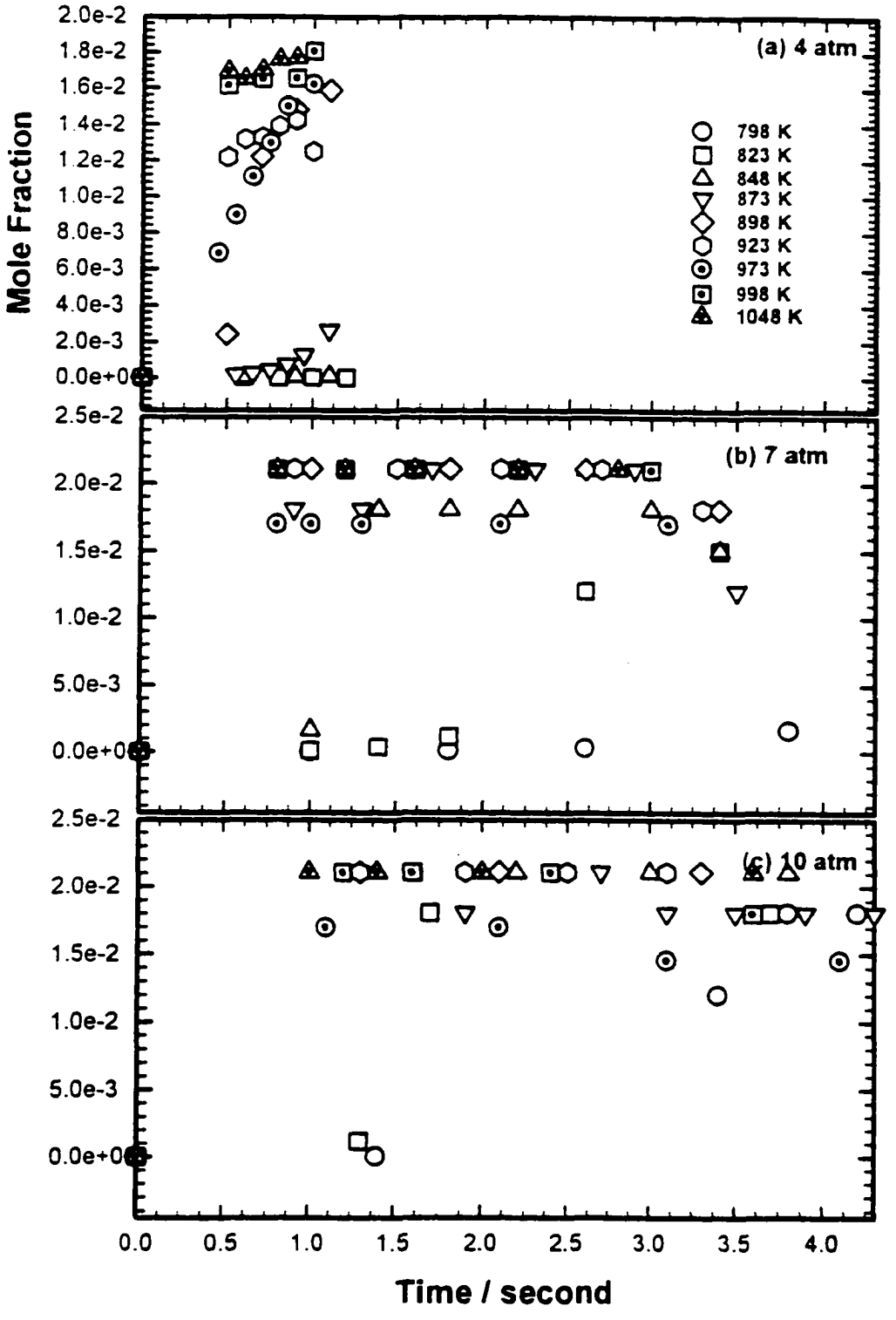


Figure IIC. 120 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CO at $\varphi = 1.50$

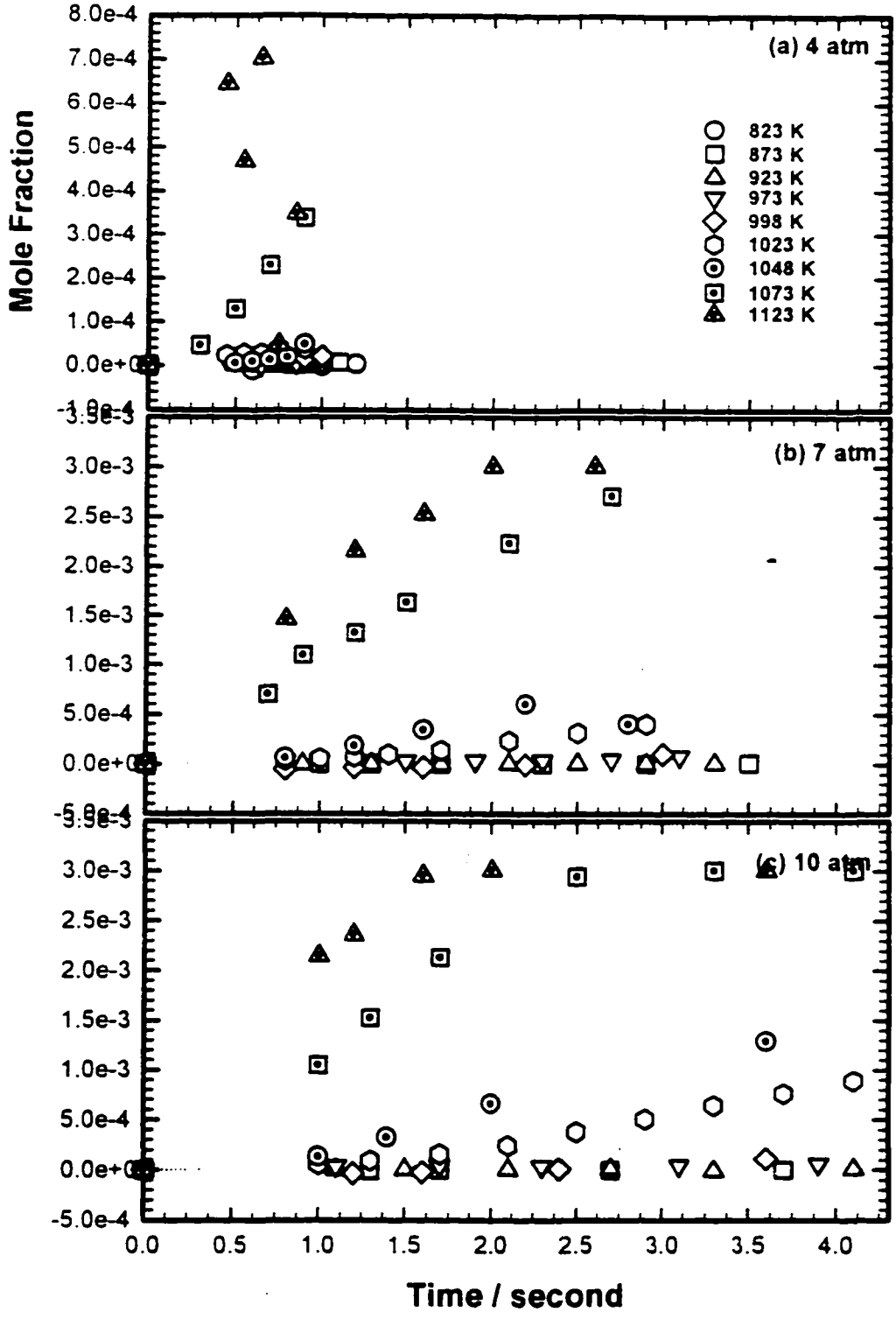


Figure IIC. 121 Experimental result of 0.5% MTBE pyrolysis: temperature and pressure dependence of CO

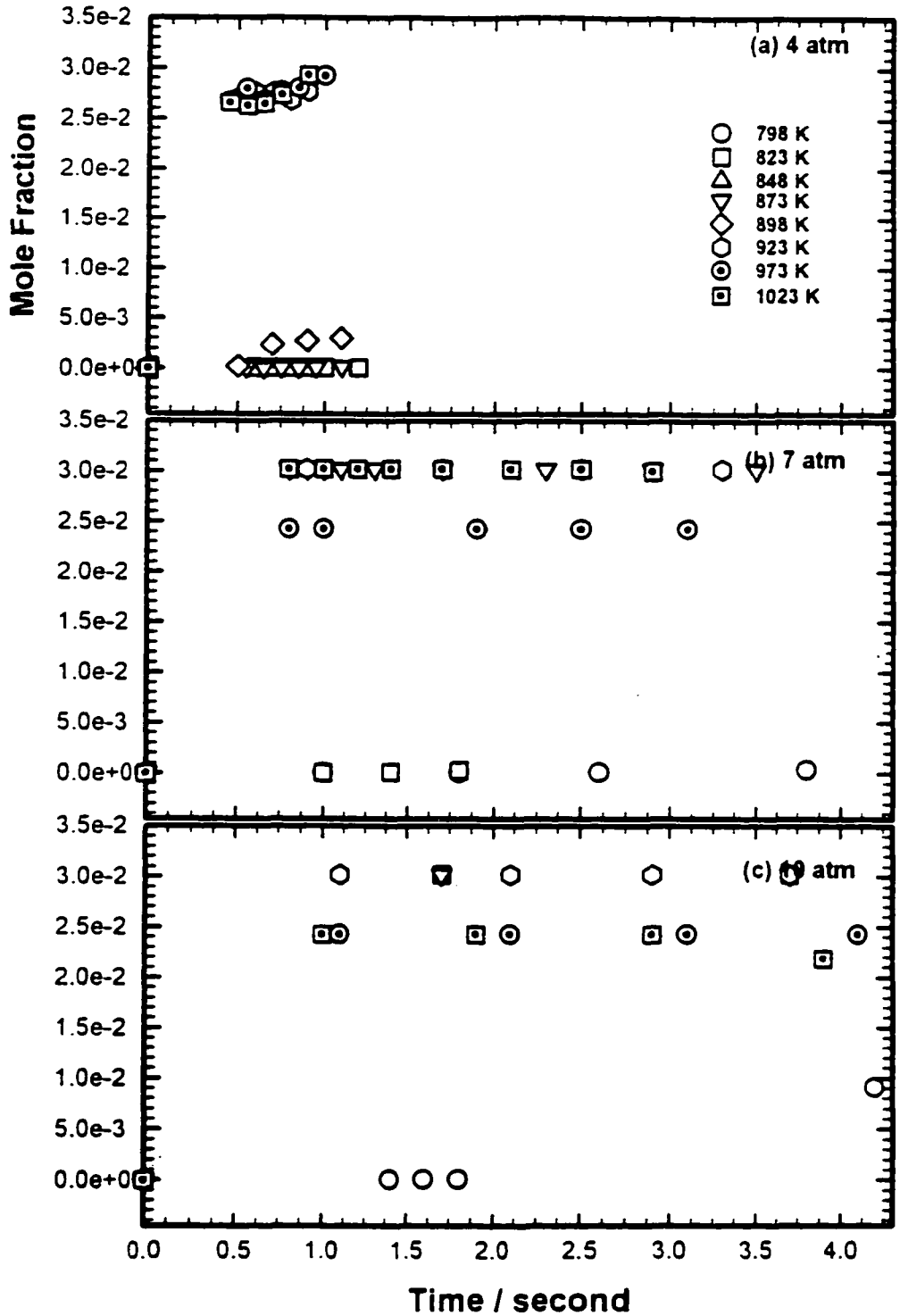


Figure IIC. 122 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CO_2 at $\varphi = 0.75$

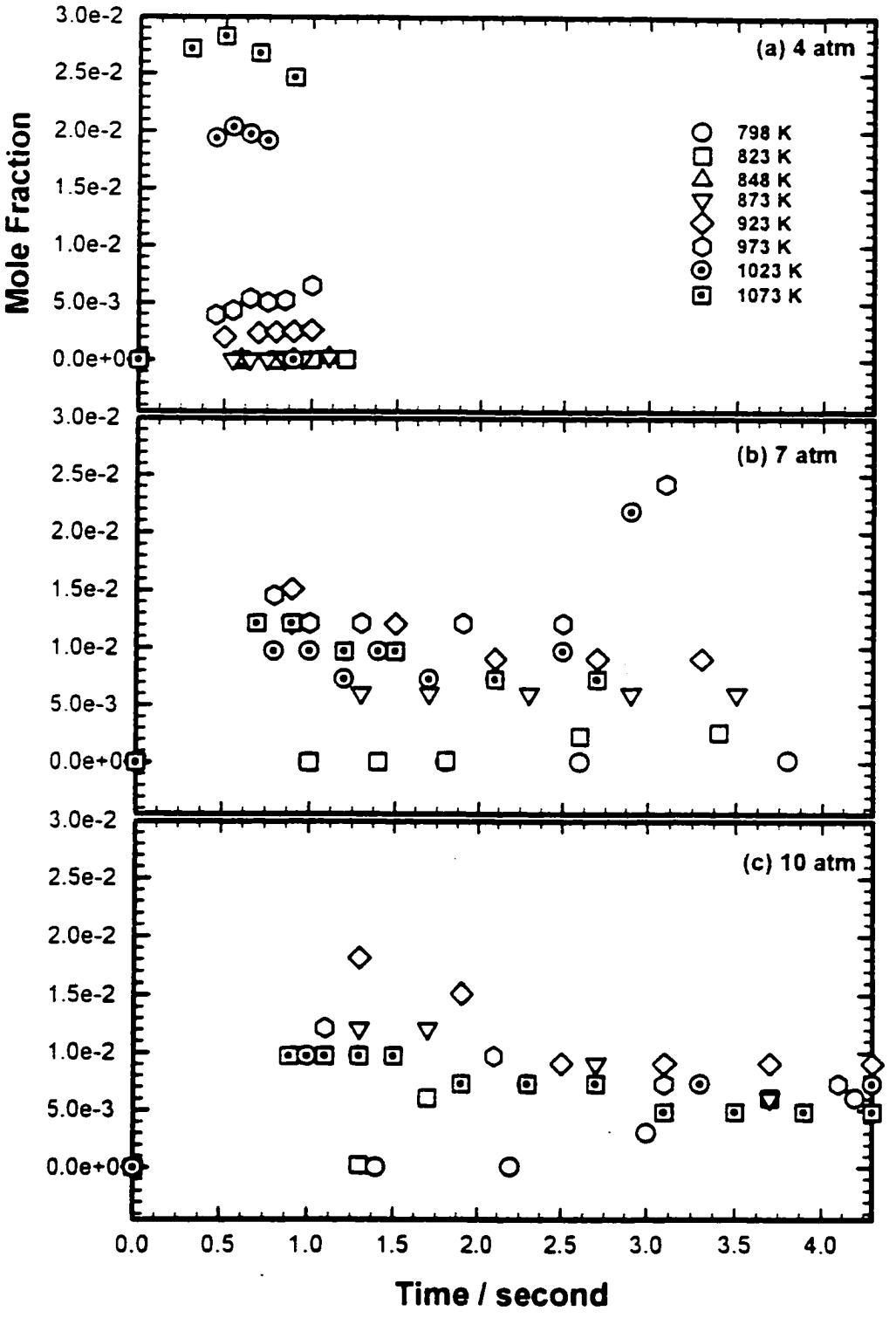


Figure IIC. 123 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CO_2 at $\varphi = 1.00$

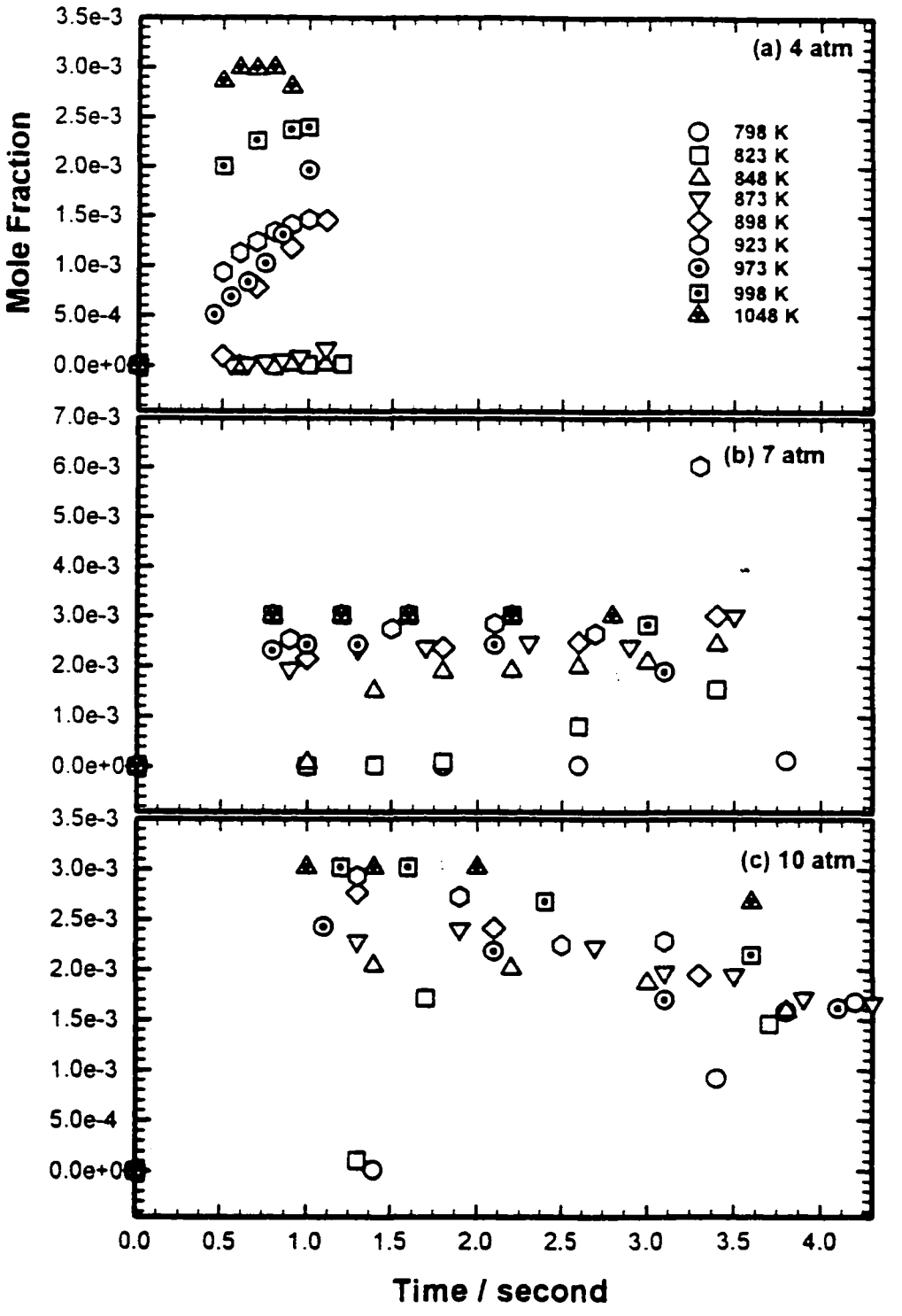
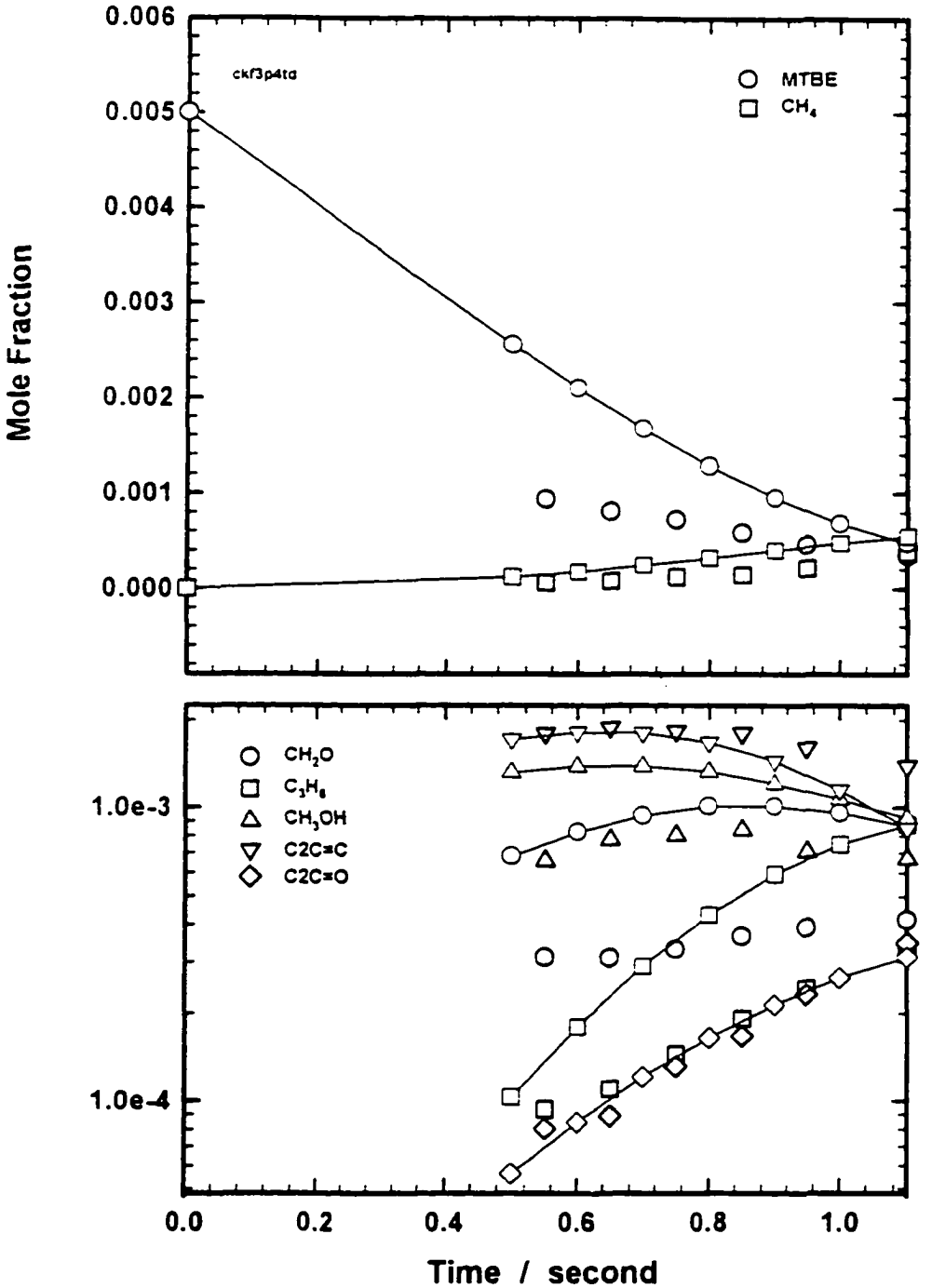
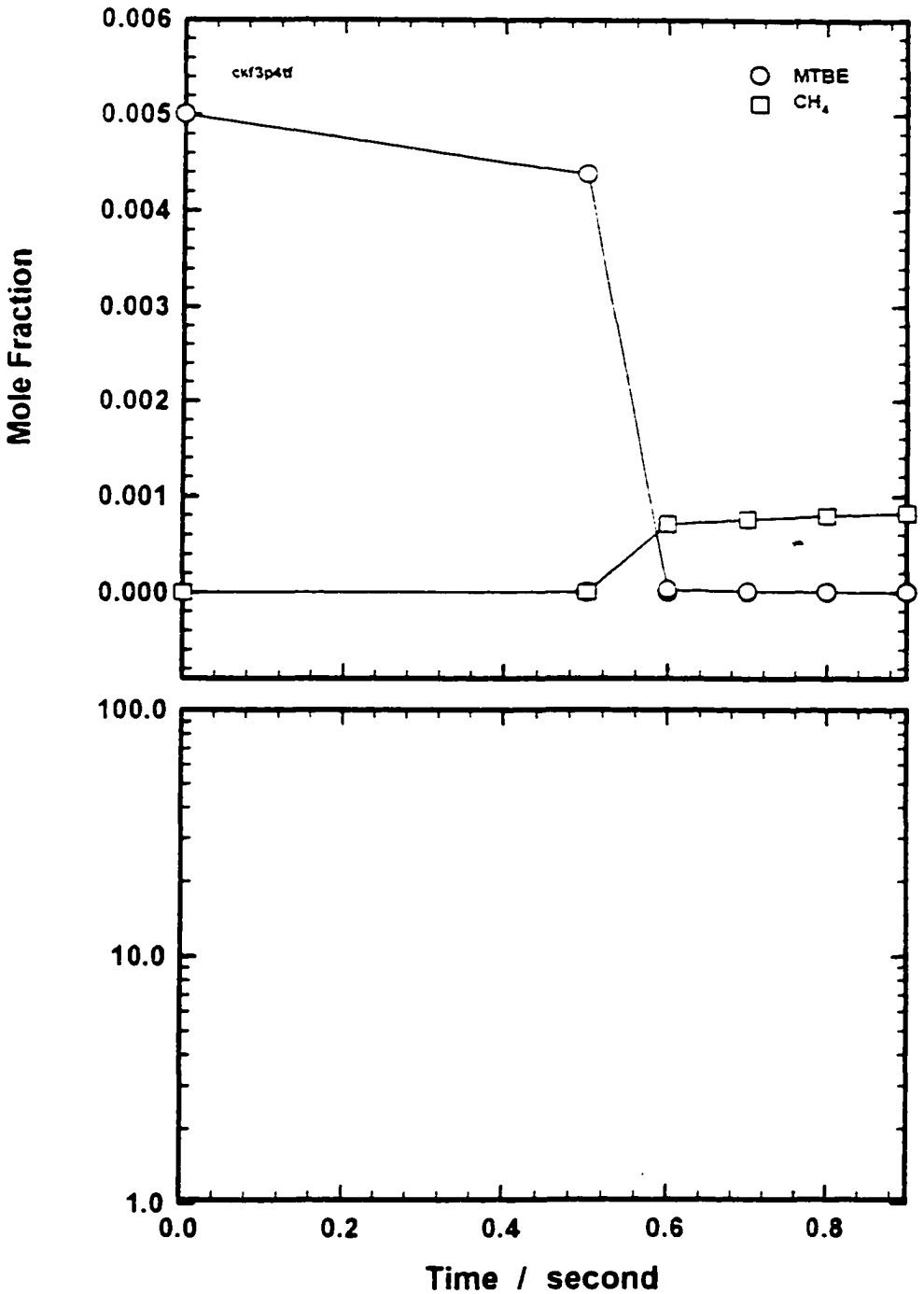


Figure IIC. 124 Experimental result of 0.5% MTBE oxidation: temperature and pressure dependence of CO_2 at $\varphi = 1.50$



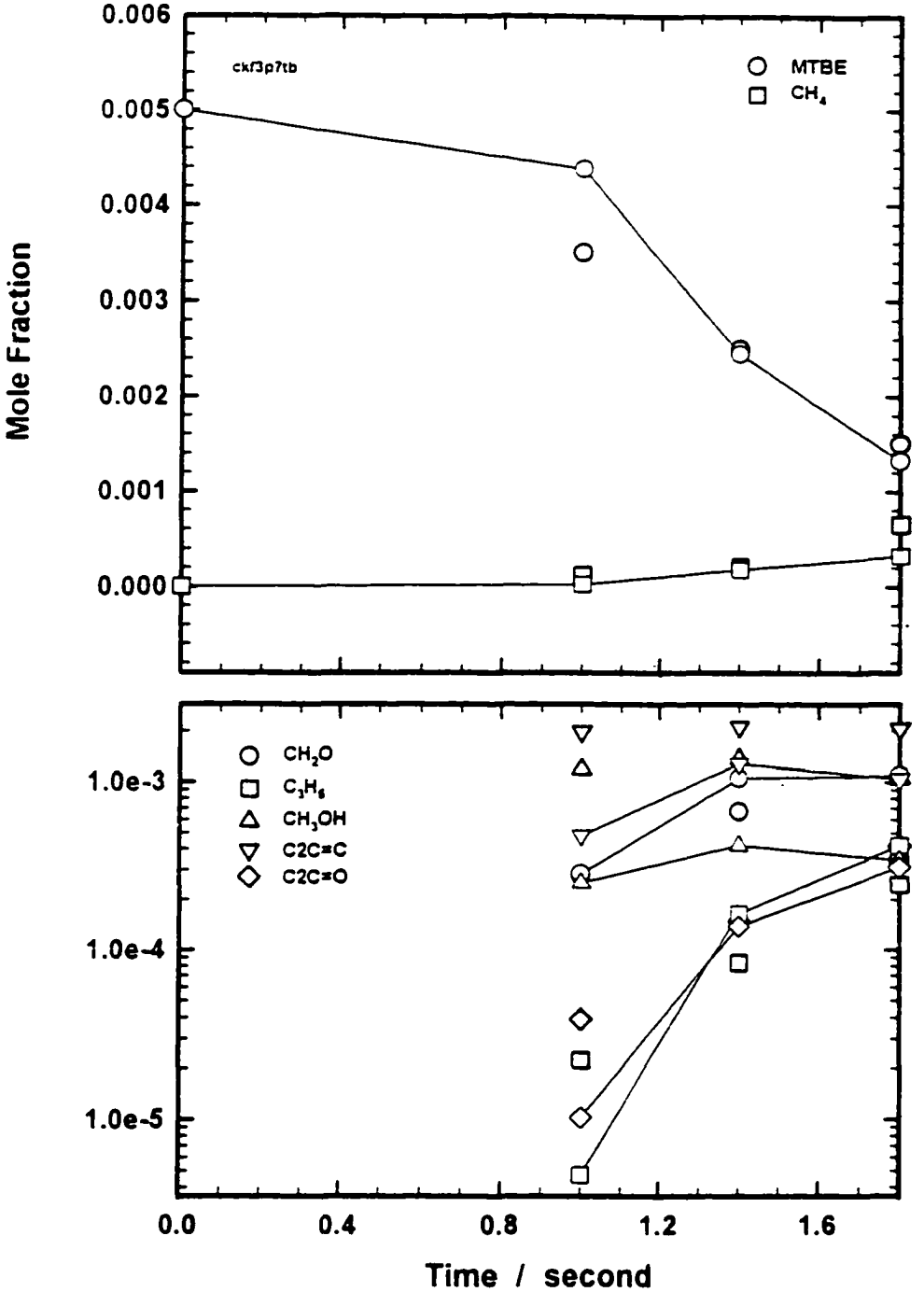
line is modeling result, symbols are experimental data

Figure ПС. 125 Comparison of experiment and modeling result
$\varphi = 0.75$, P = 4 atm, T = 873 K



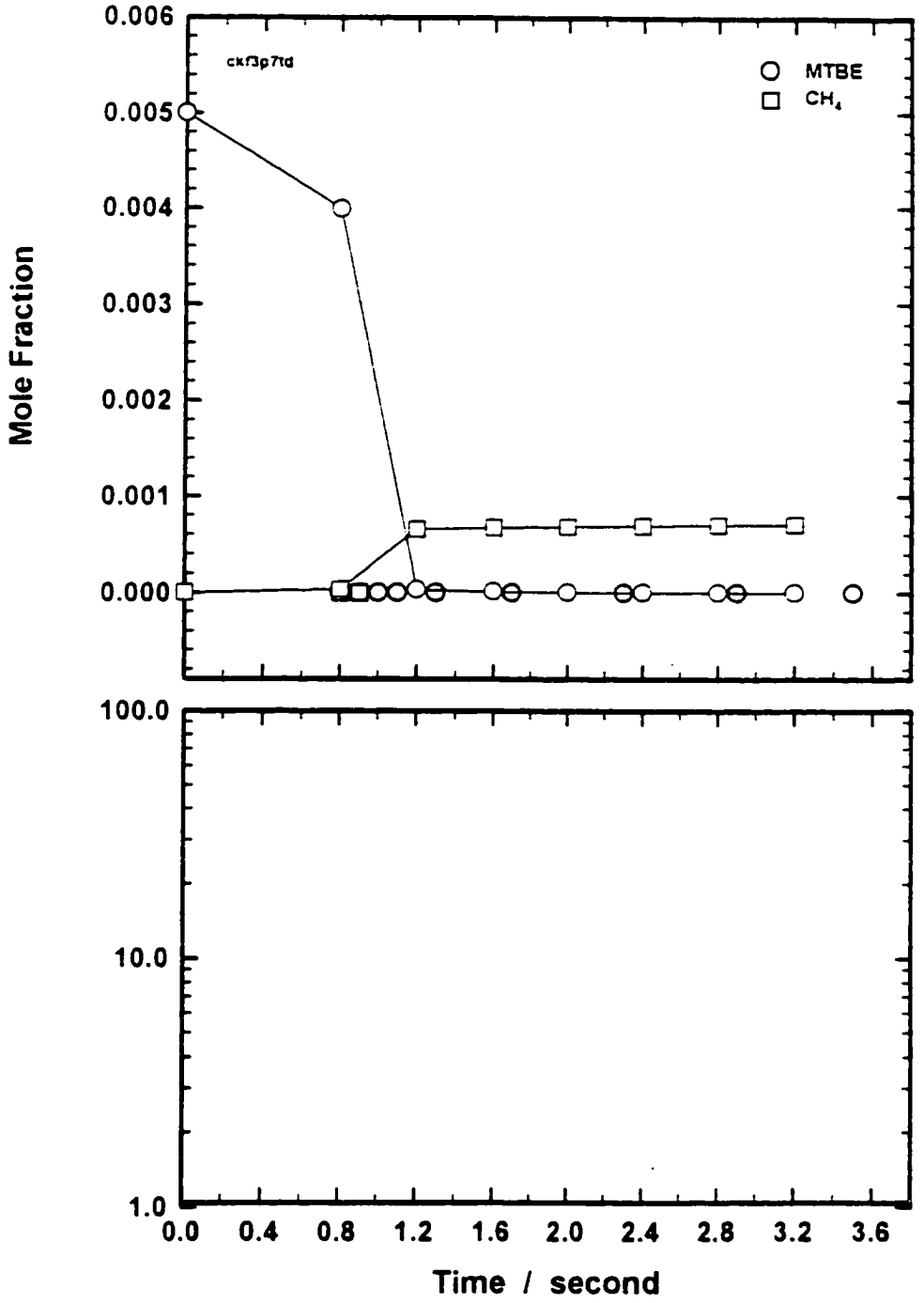
line is modeling result, symbols are experimental data

Figure IIC. 126 Comparison of experiment and modeling result
$\varphi = 0.75$, P = 4 atm, T = 923 K



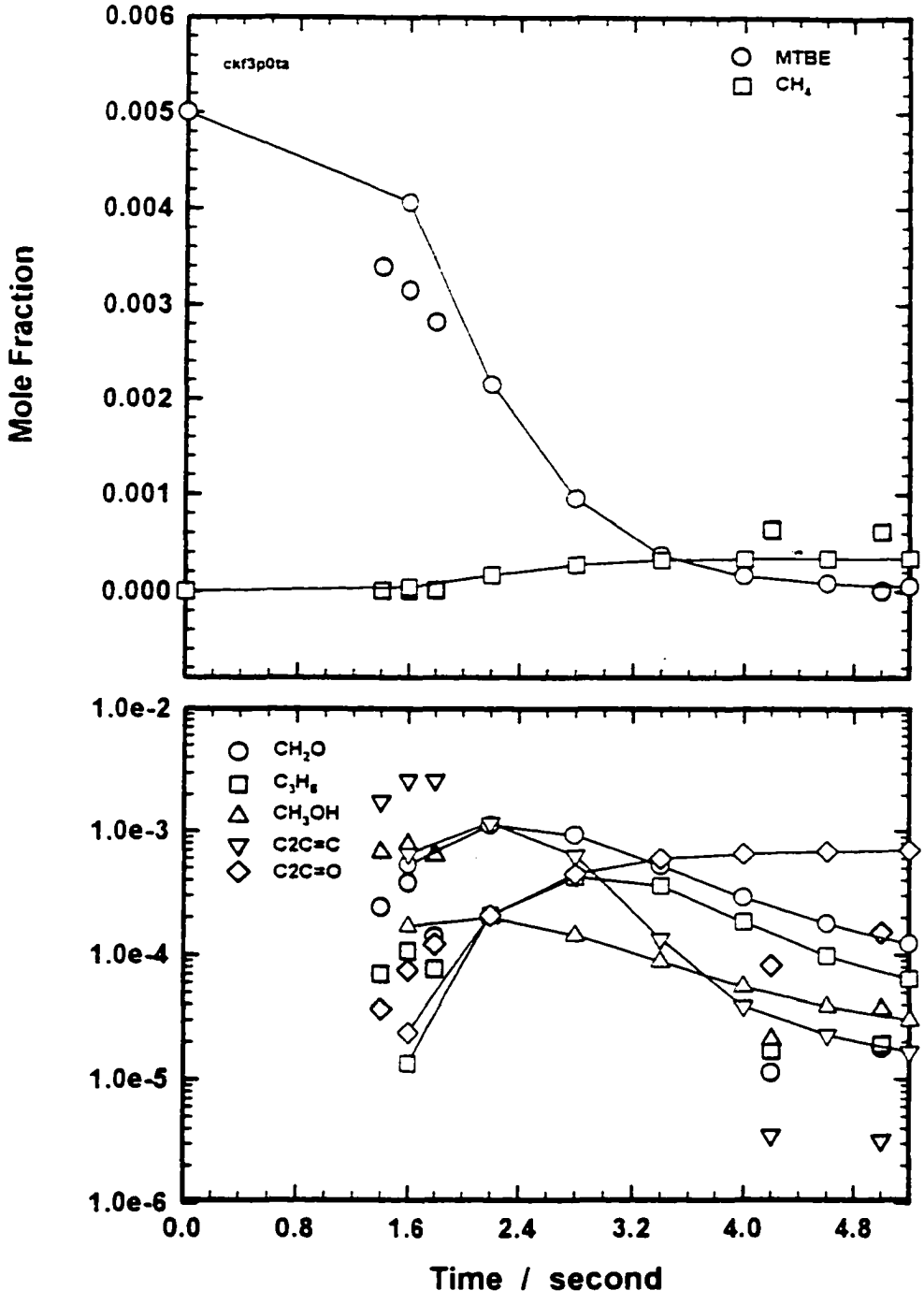
line is modeling result, symbols are experimental data

Figure IIC. 127 Comparison of experiment and modeling result
$\varphi = 0.75$, P = 7 atm, T = 823 K



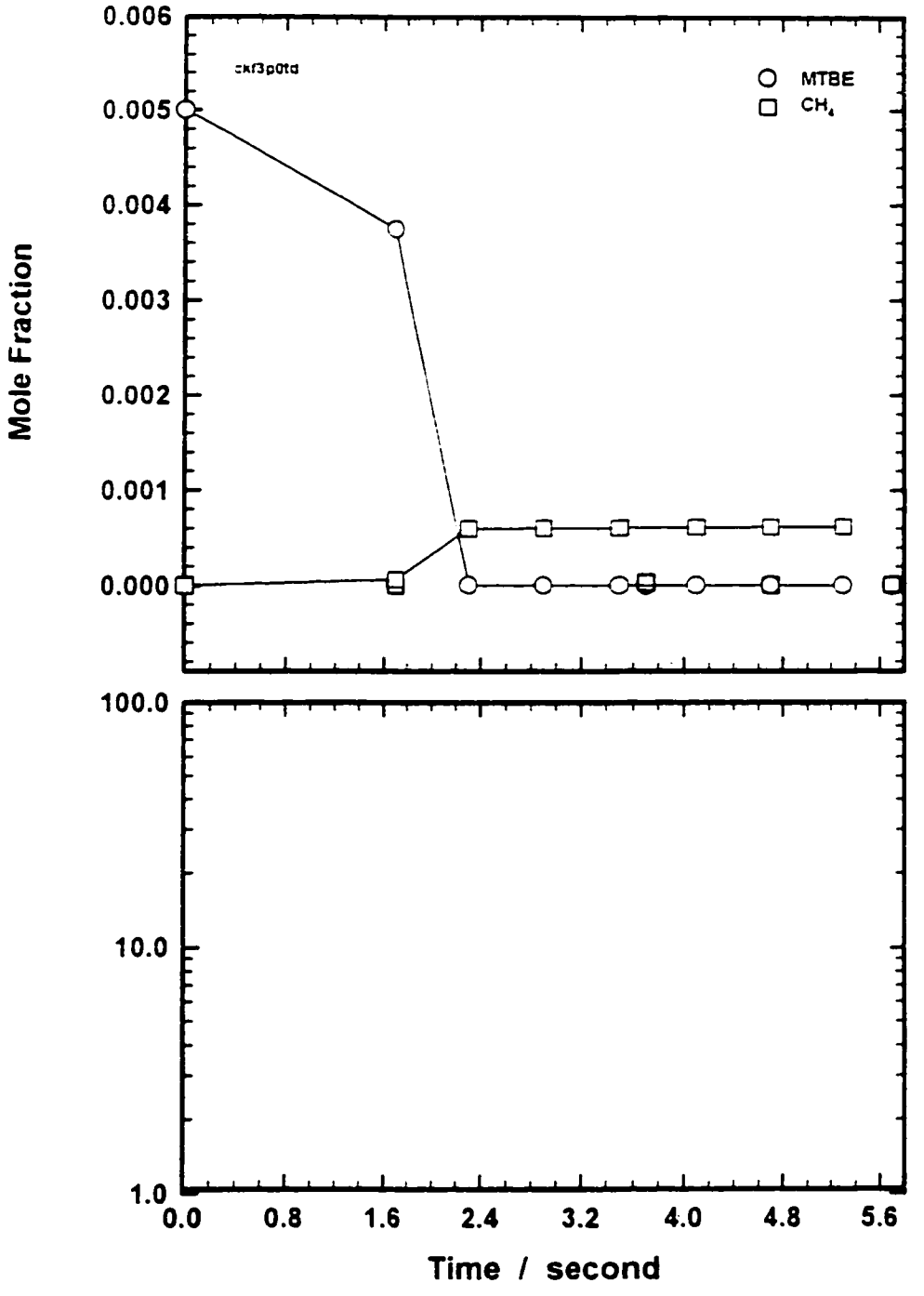
line is modeling result, symbols are experimental data

Figure IIC. 128 Comparison of experiment and modeling result
$\varphi = 0.75$, P = 7 atm, T = 873 K



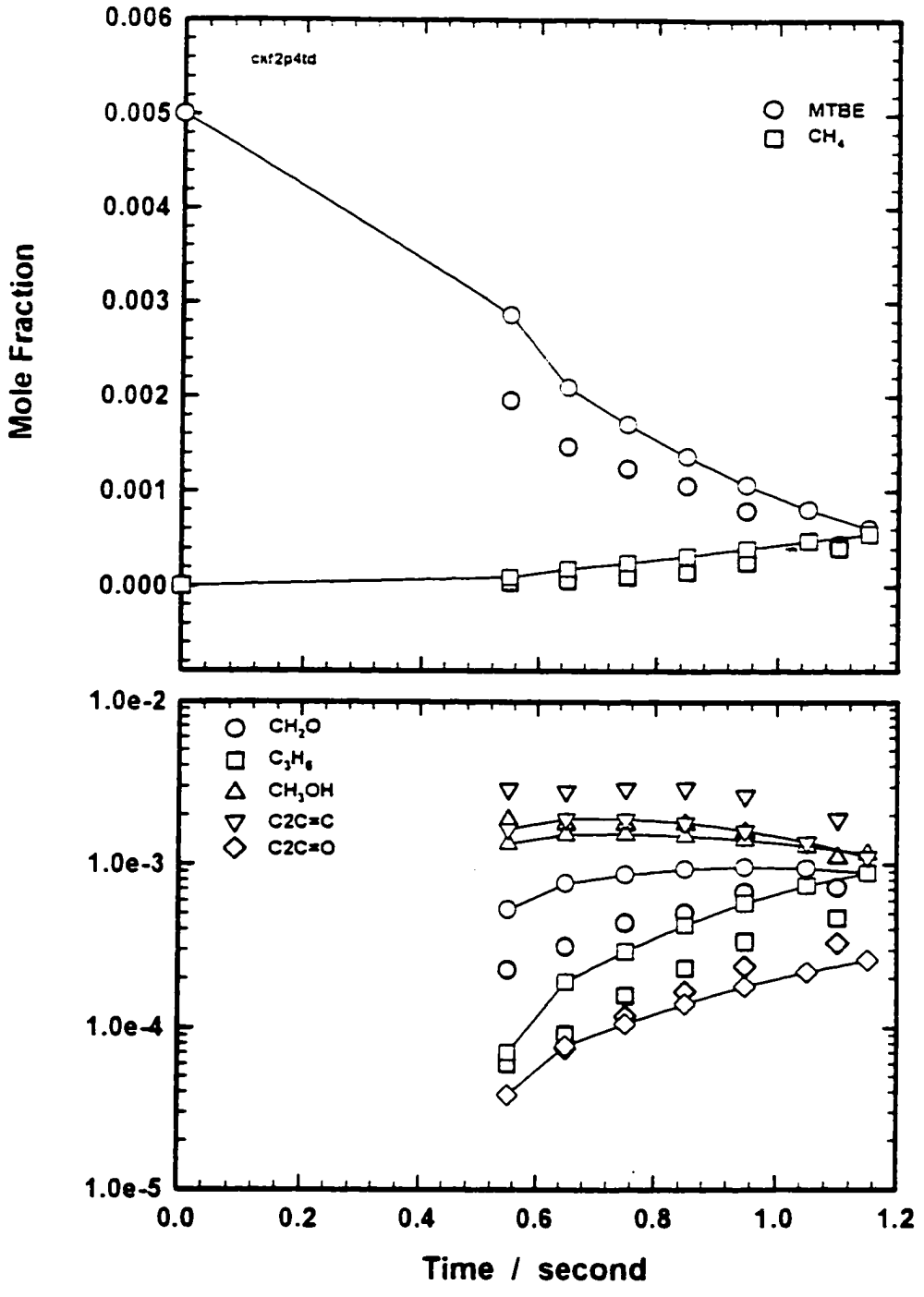
line is modeling result, symbols are experimental data

Figure IIC. 129 Comparison of experiment and modeling result
$\varphi = 0.75$, P = 10 atm, T = 798 K



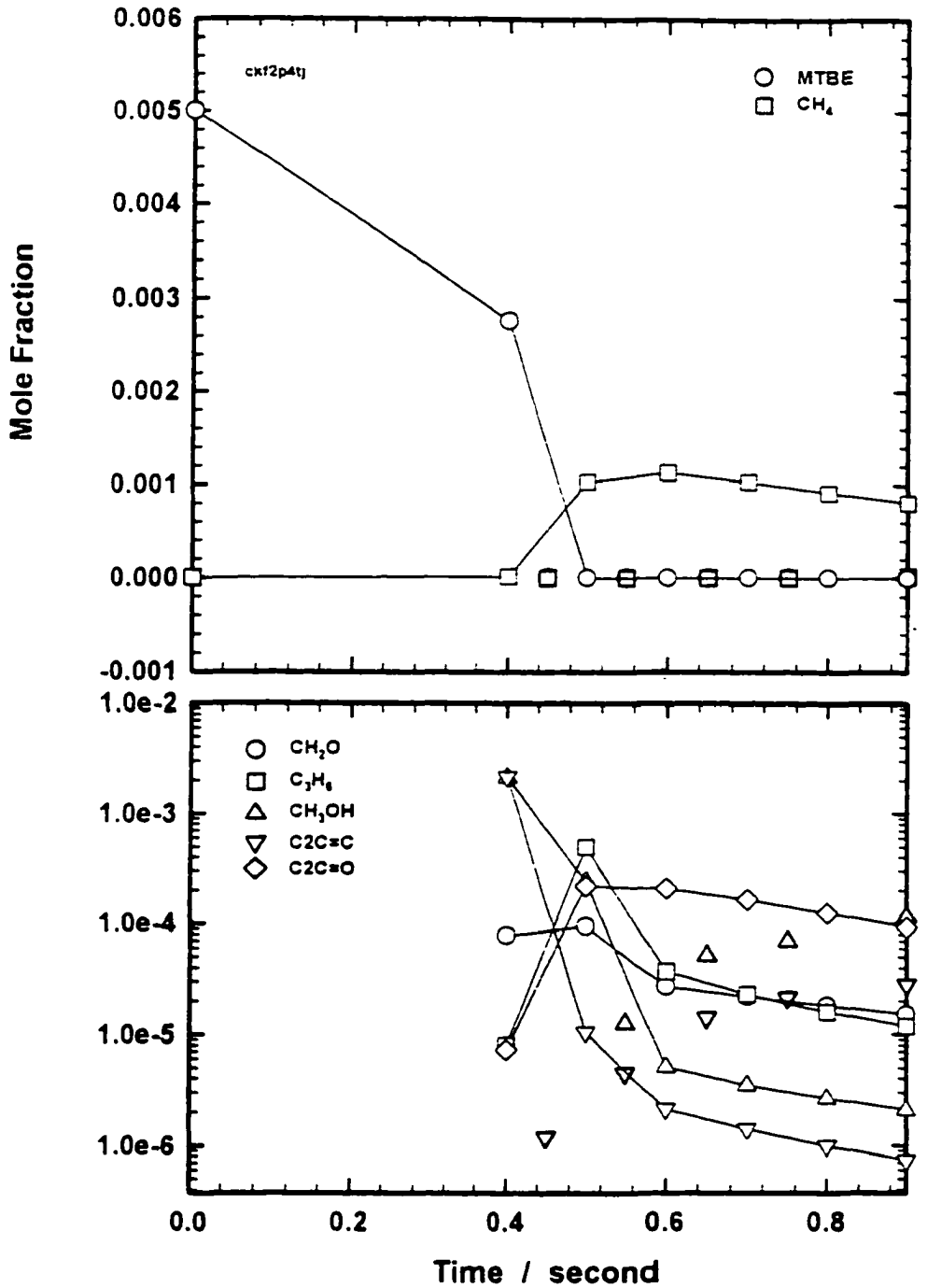
line is modeling result, symbols are experimental data

Figure IIC. 130 Comparison of experiment and modeling result
$\varphi = 0.75$, P = 10 atm, T = 873 K



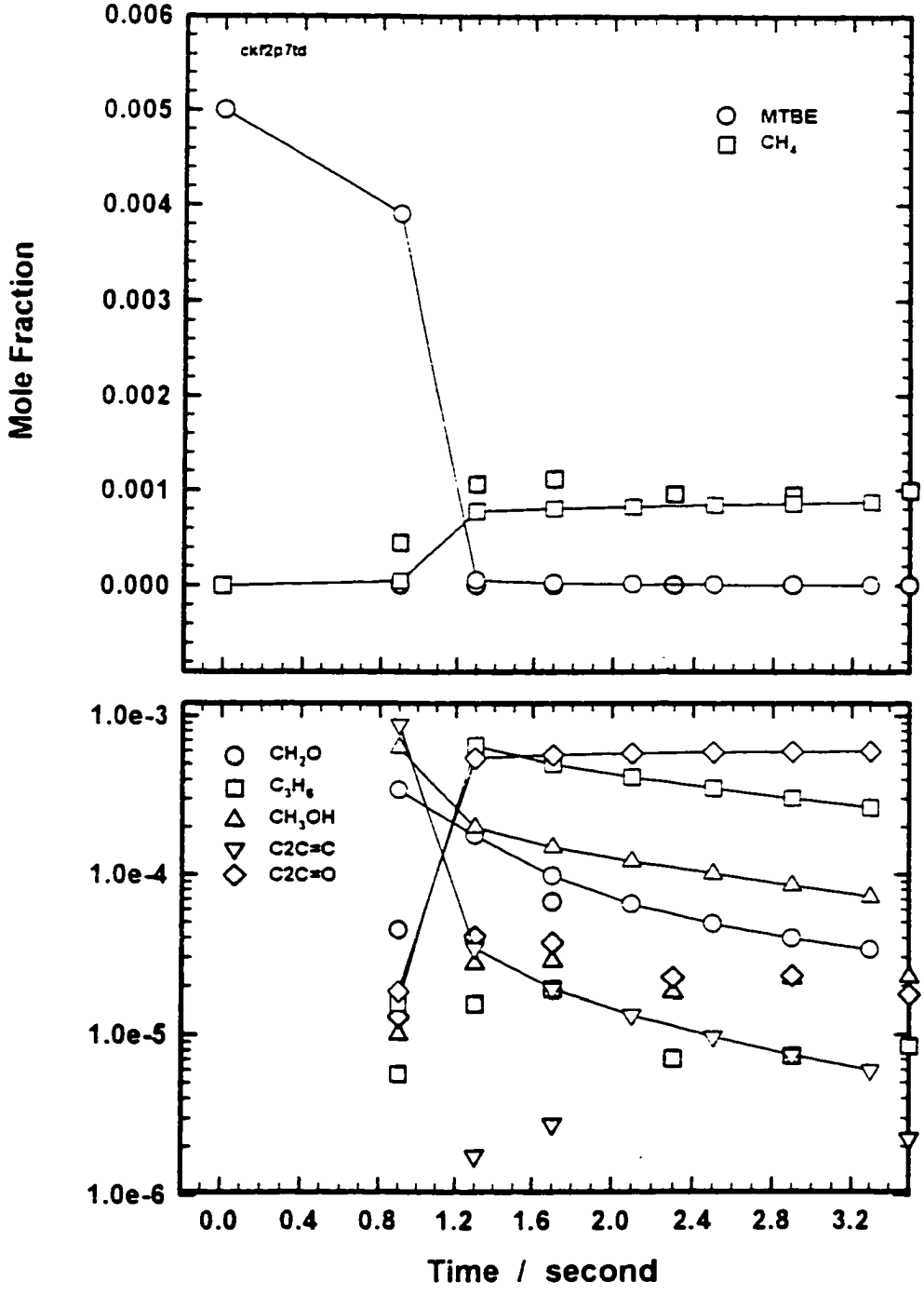
line is modeling result, symbols are experimental data

Figure IIC. 131 Comparison of experiment and modeling result
φ = 1.0, P = 4 atm, T = 873 K



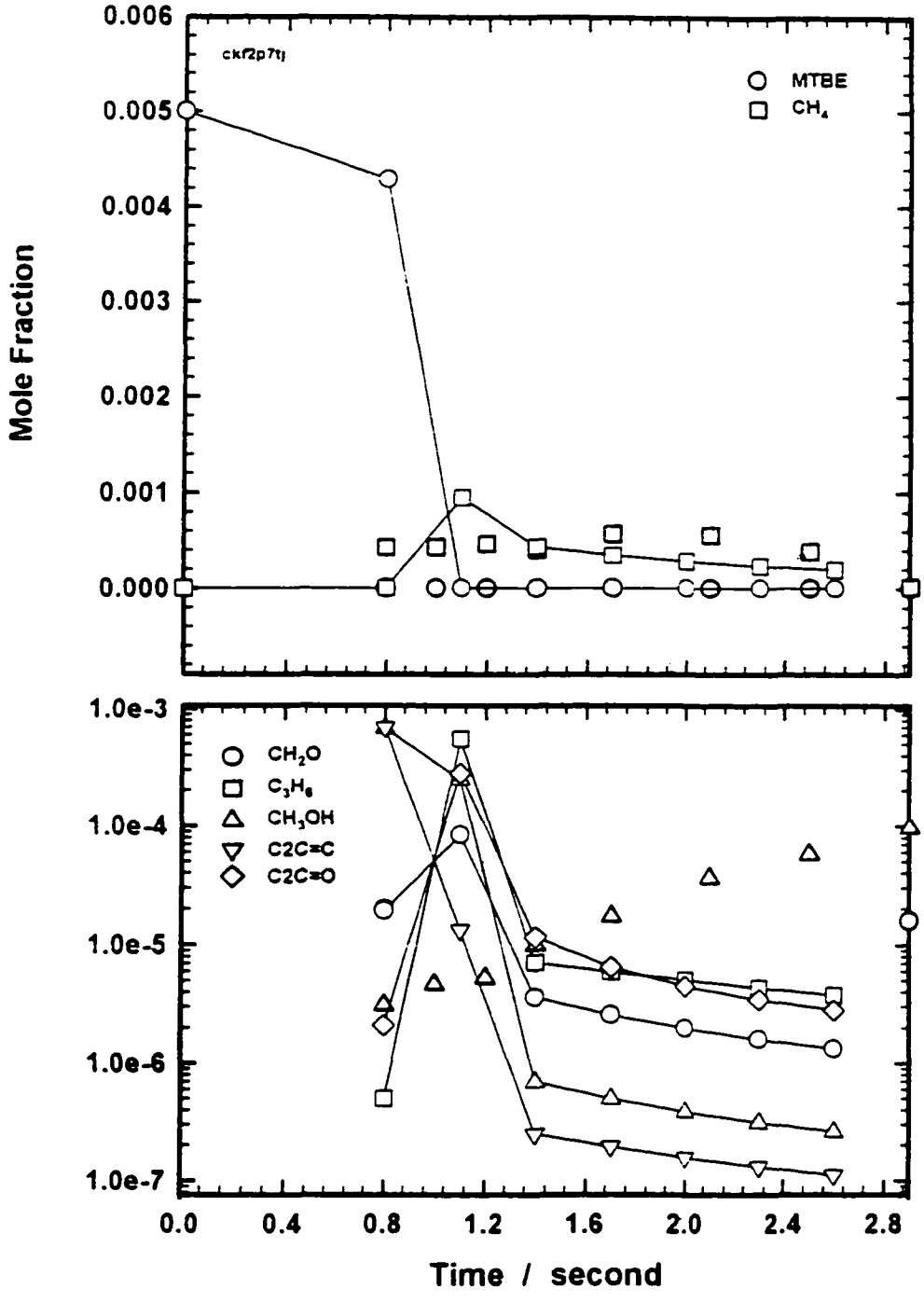
line is modeling result, symbols are experimental data

Figure IIC. 132 Comparison of experiment and modeling result
φ = 1.0, P = 4 atm, T = 1023 K



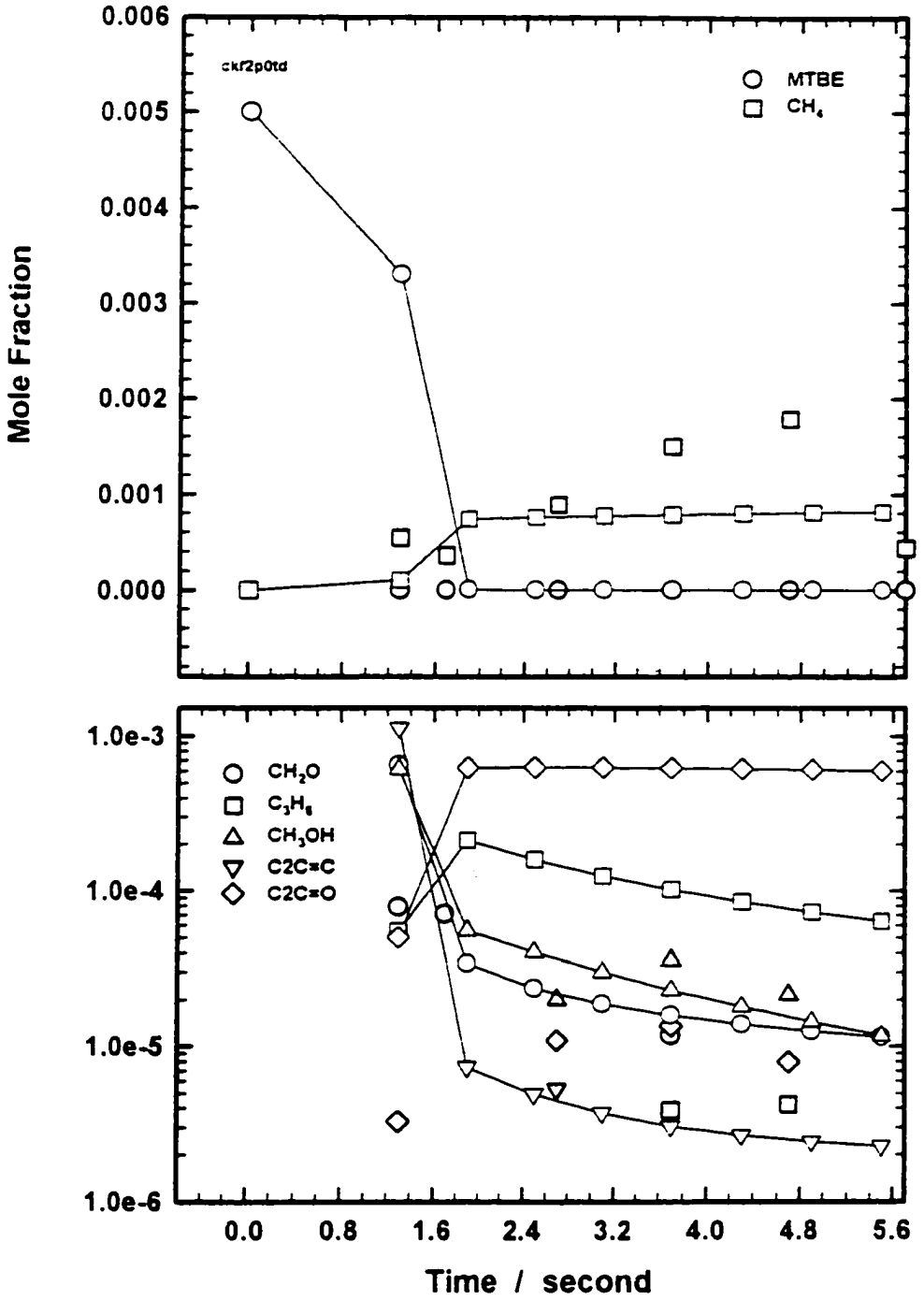
line is modeling result, symbols are experimental data

Figure IIC. 133 Comparison of experiment and modeling result
φ = 1.0, P = 7 atm, T = 873 K



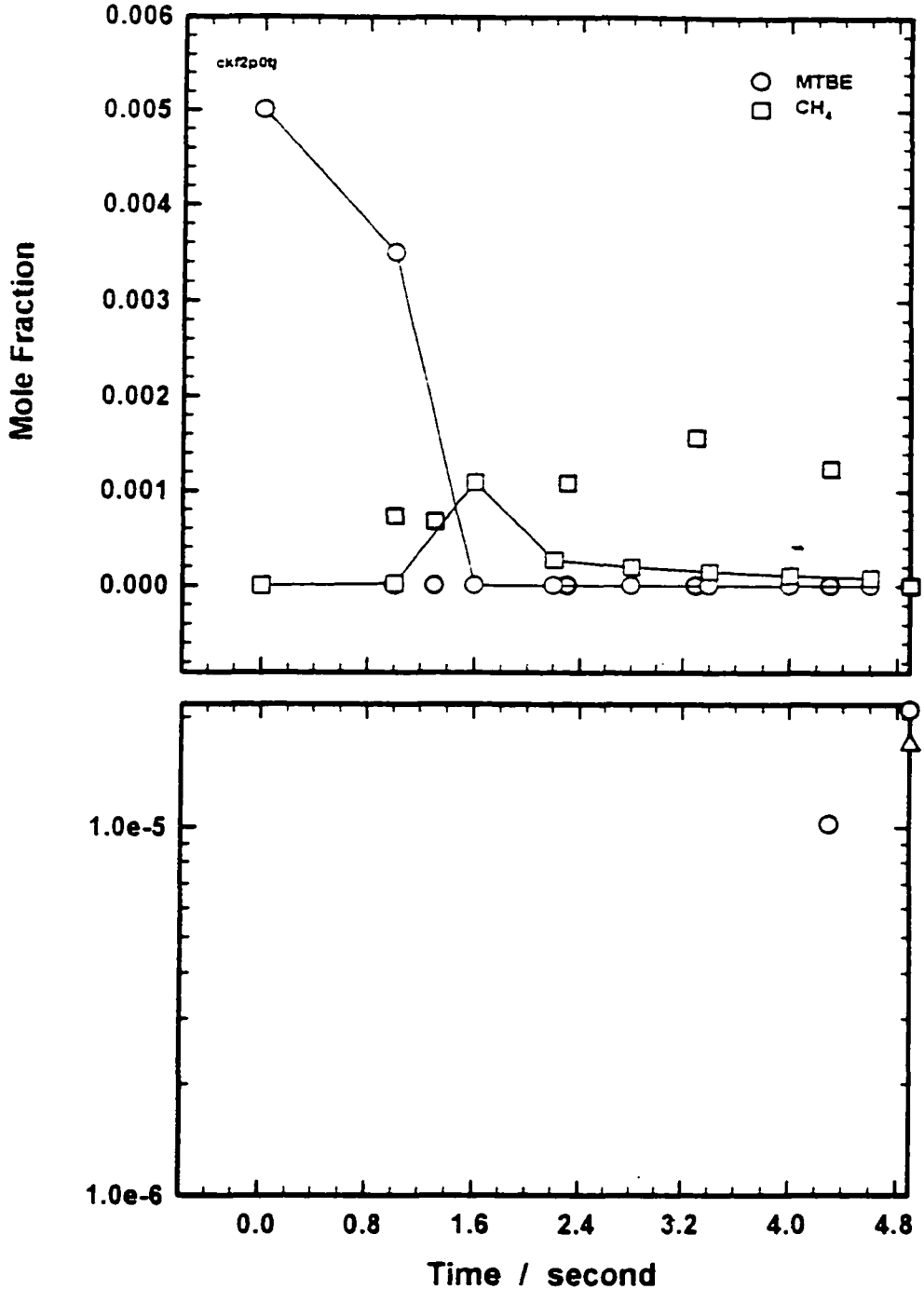
line is modeling result, symbols are experimental data

Figure IIC. 134 Comparison of experiment and modeling result
φ = 1.0, P = 7 atm, T = 1023 K



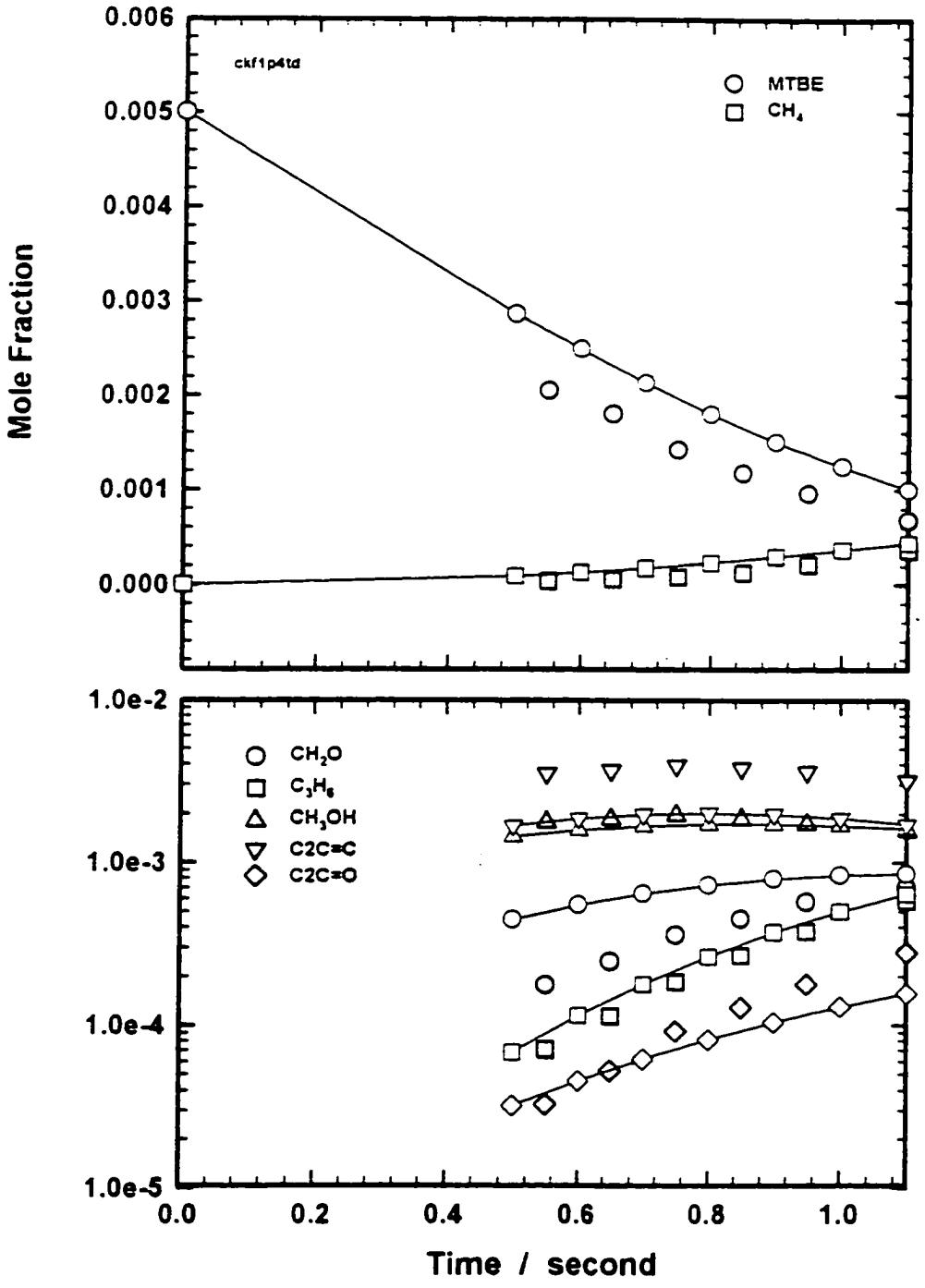
line is modeling result, symbols are experimental data

Figure IIC. 135 Comparison of experiment and modeling result
φ = 1.0, P = 10 atm, T = 873 K



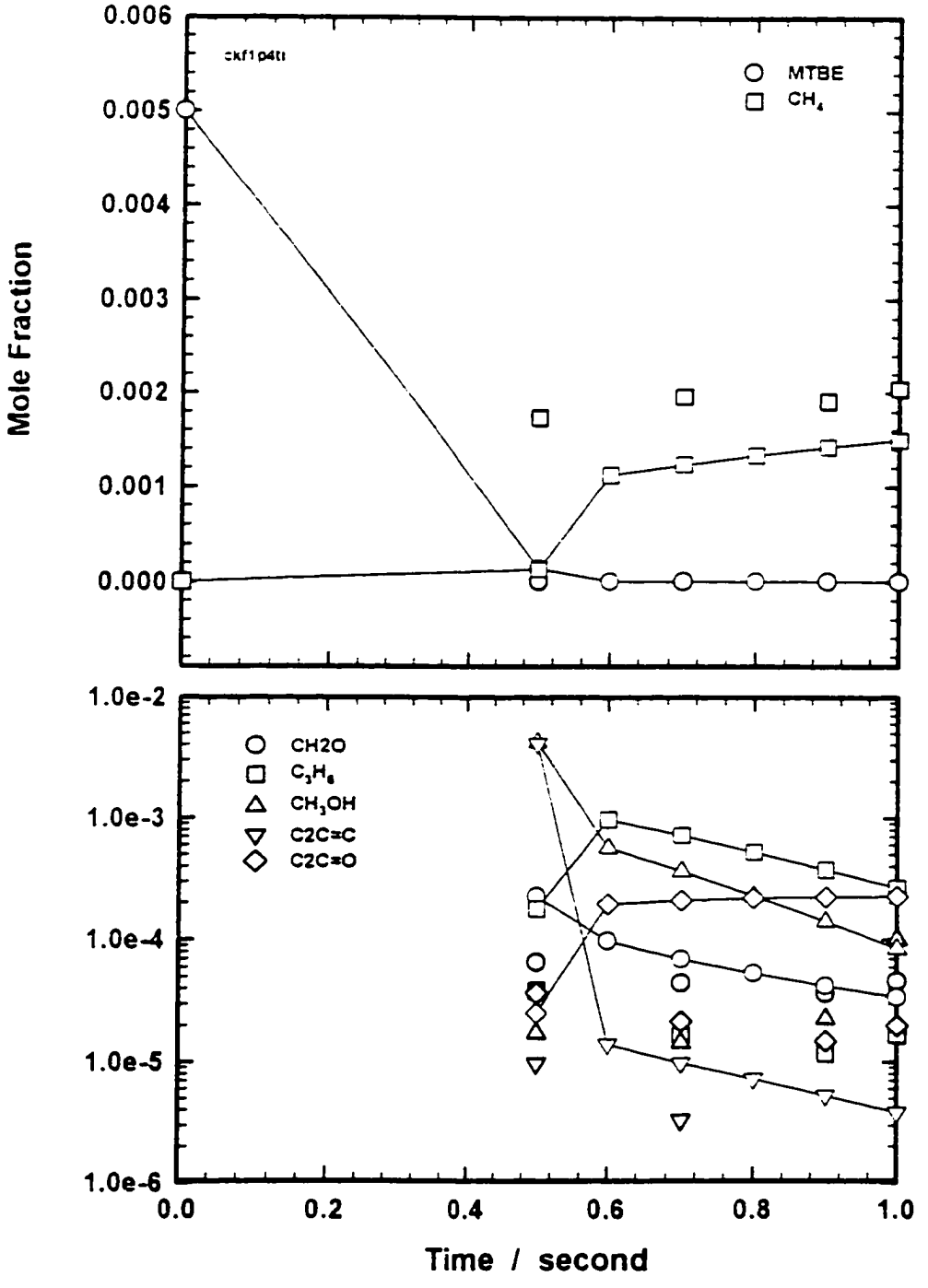
line is modeling result, symbols are experimental data

Figure IIC. 136 Comparison of experiment and modeling result
φ = 1.0, P = 10 atm, T = 1023 K



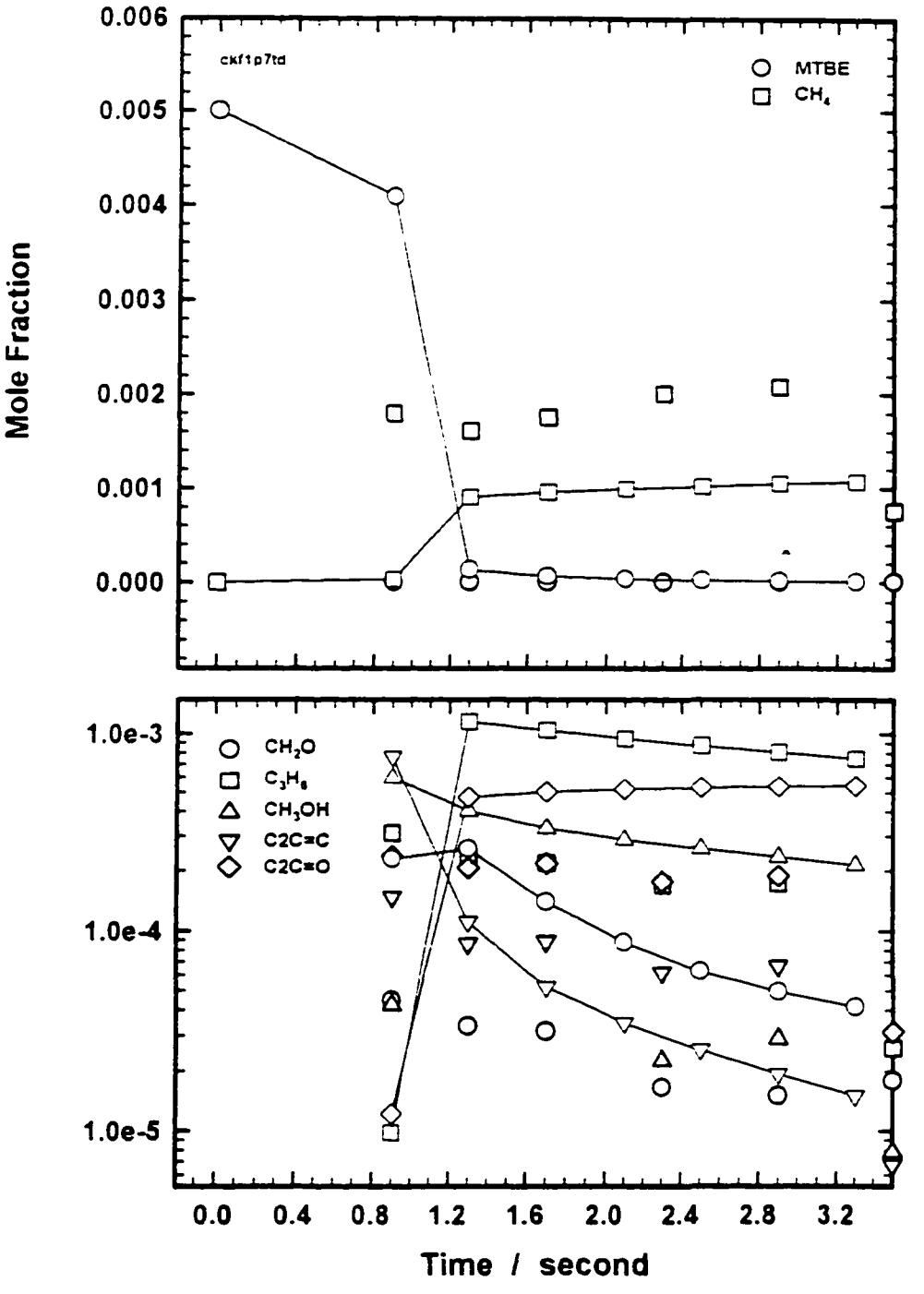
line is modeling result, symbols are experimental data

Figure IIC. 137 Comparison of experiment and modeling result
φ = 1.5, P = 4 atm, T = 873 K



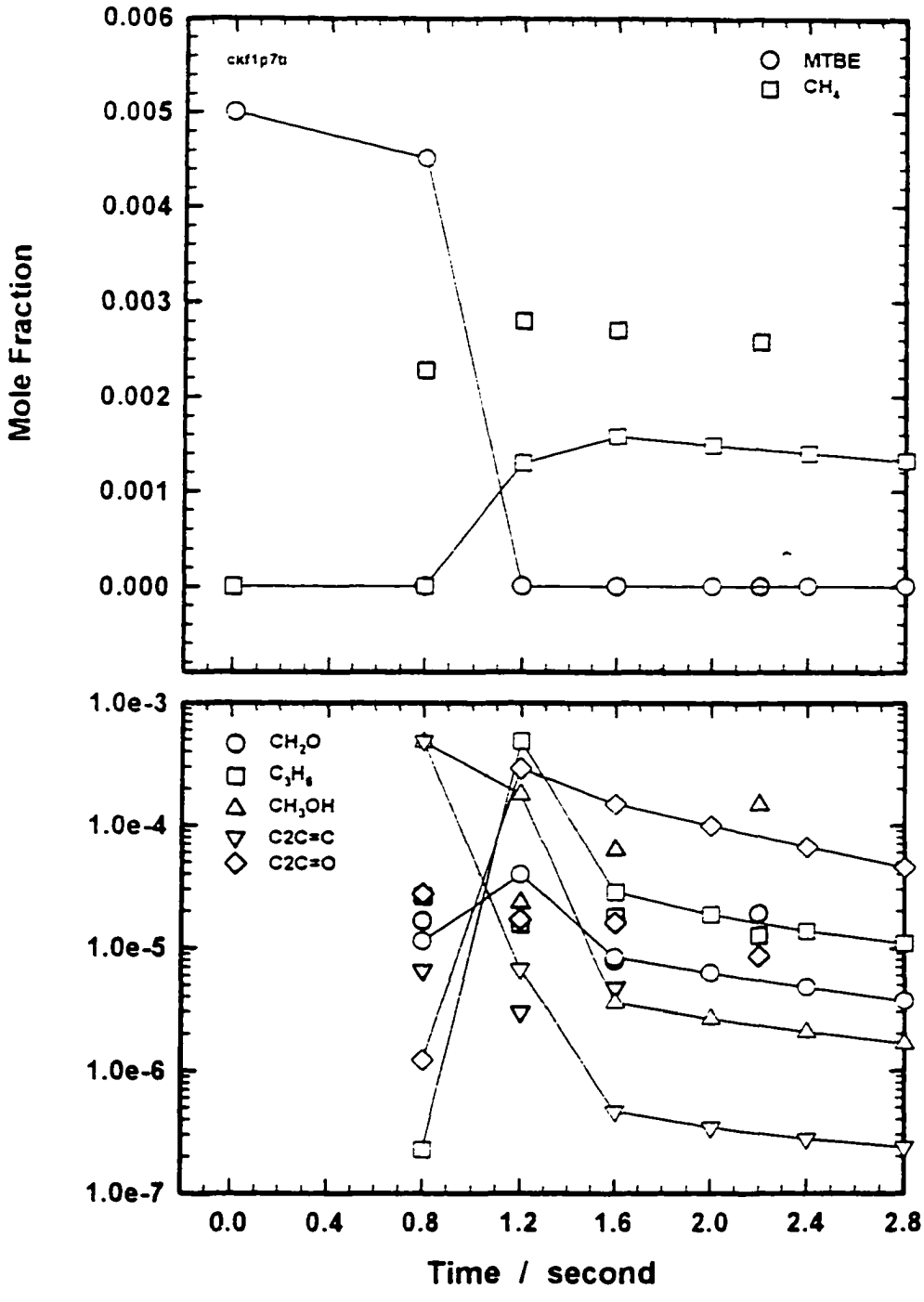
line is modeling result, symbols are experimental data

Figure IIC. 138 Comparison of experiment and modeling result
φ = 1.5, P = 4 atm, T = 998 K



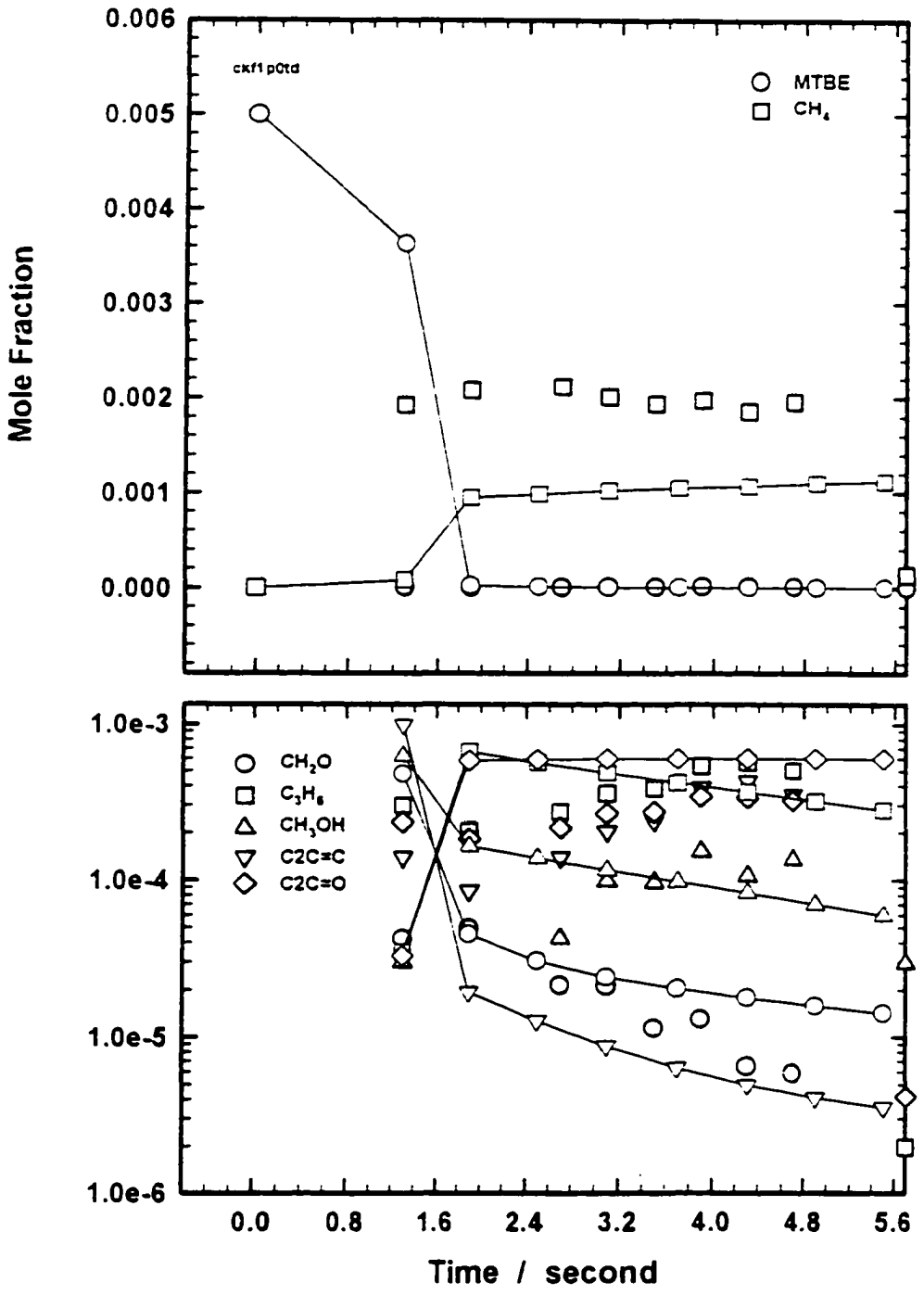
line is modeling result, symbols are experimental data

Figure IIC. 139 Comparison of experiment and modeling result
φ = 1.5, P = 7 atm, T = 873 K



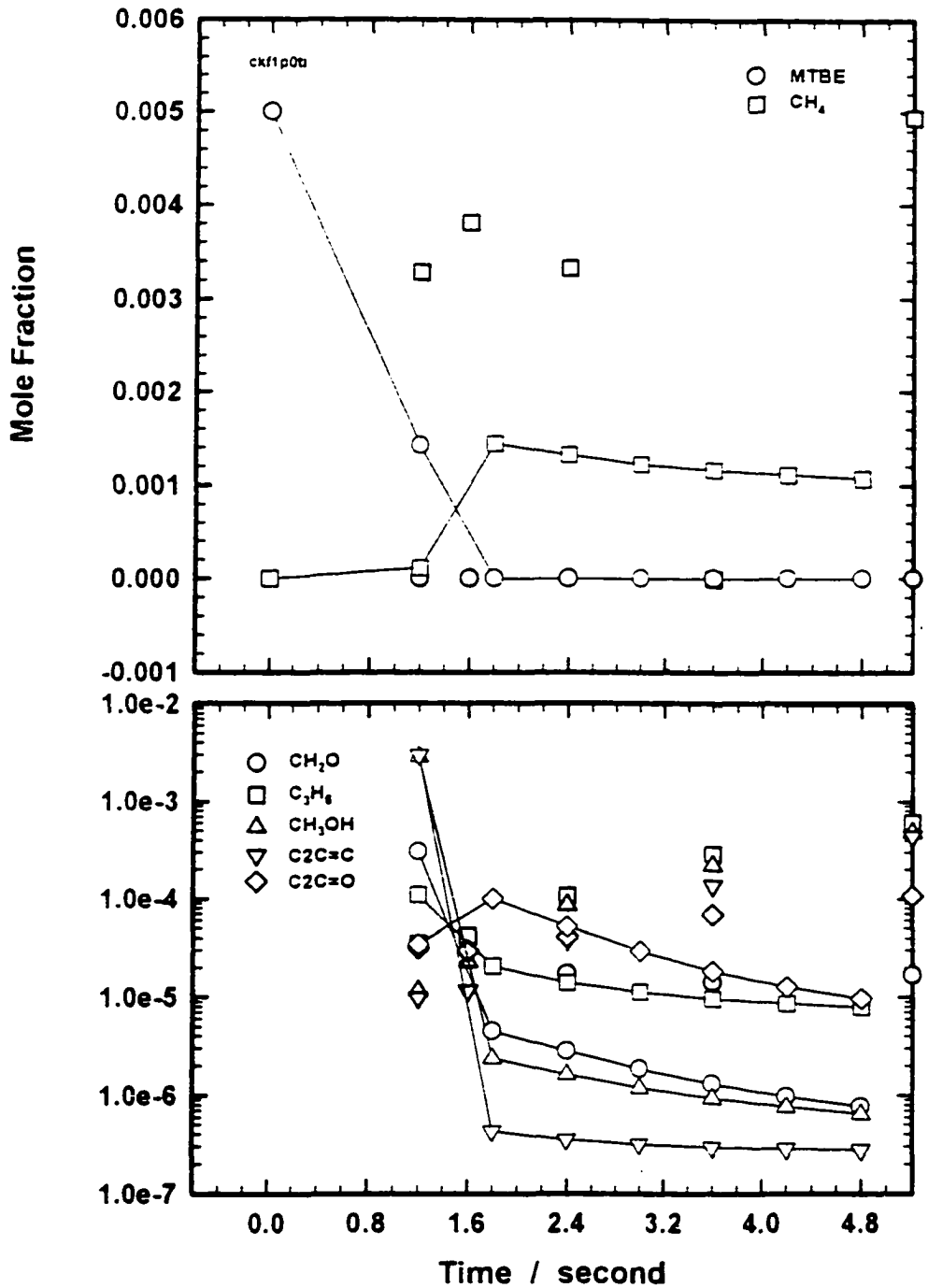
line is modeling result, symbols are experimental data

Figure IIC. 140 Comparison of experiment and modeling result
φ = 1.5, P = 7 atm, T = 998 K



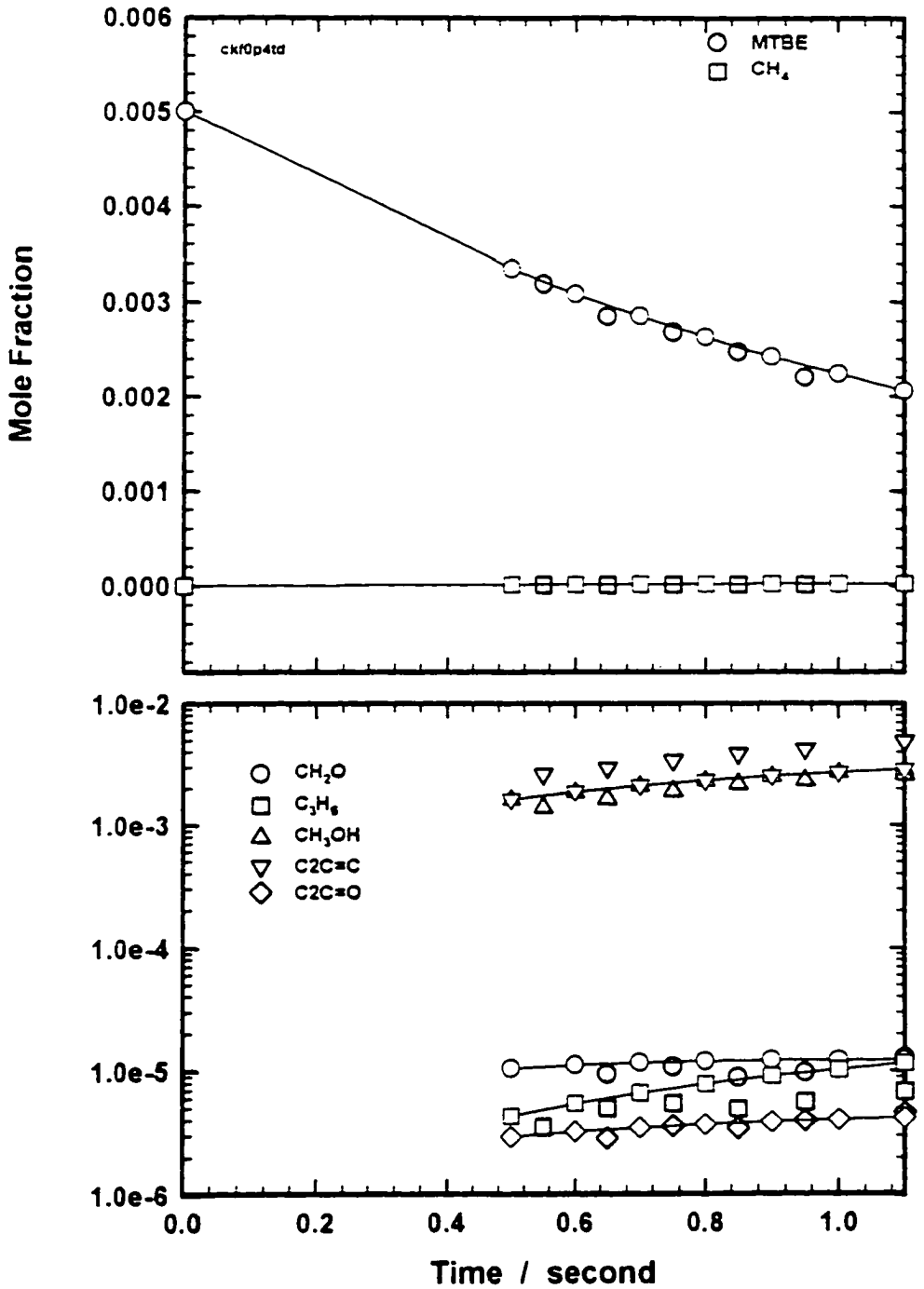
line is modeling result, symbols are experimental data

Figure IIC. 141 Comparison of experiment and modeling result
φ = 1.5, P = 10 atm, T = 873 K



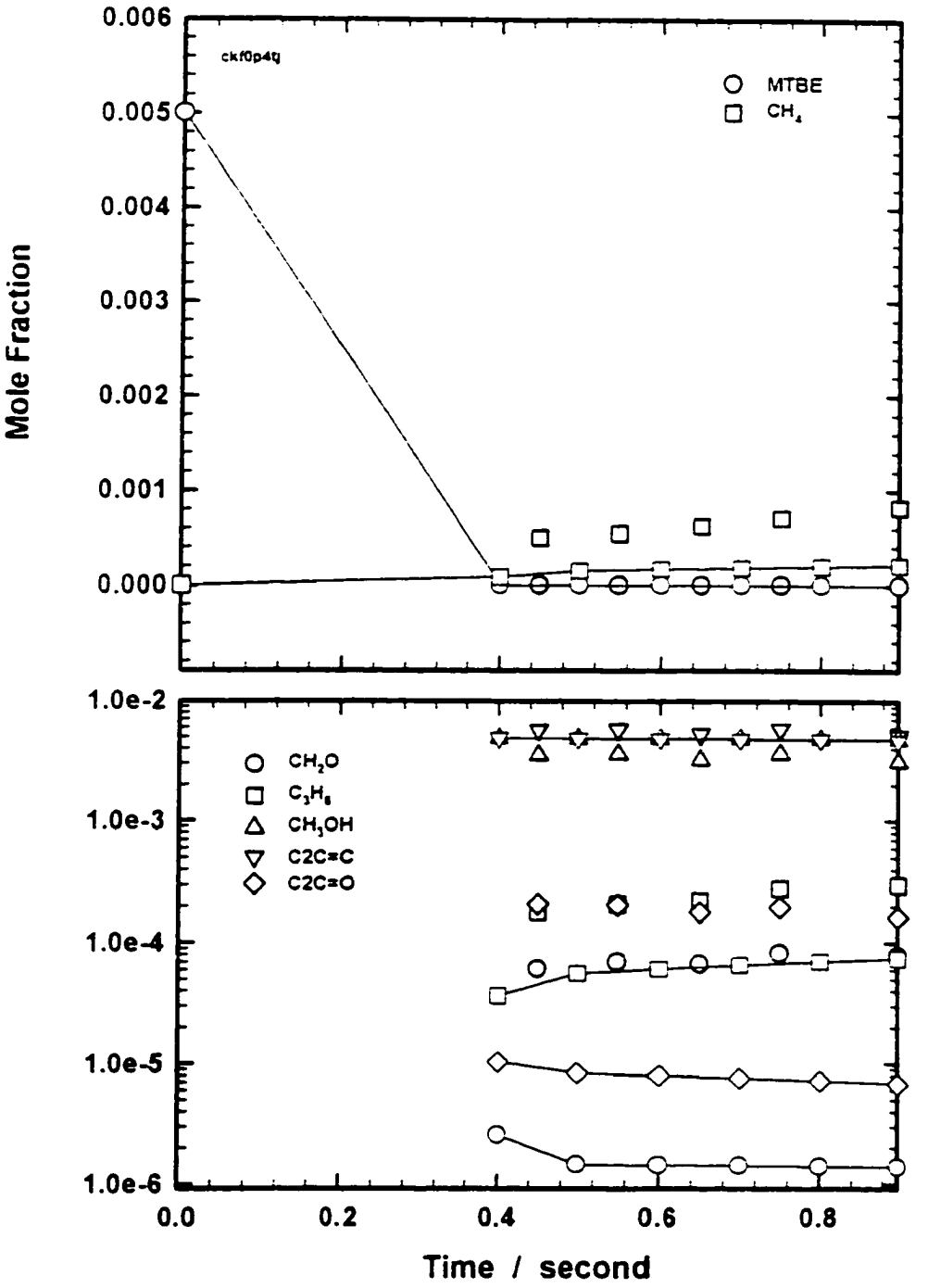
line is modeling result, symbols are experimental data

Figure IIC. 142 Comparison of experiment and modeling result
φ = 1.5, P = 10 atm, T = 998 K



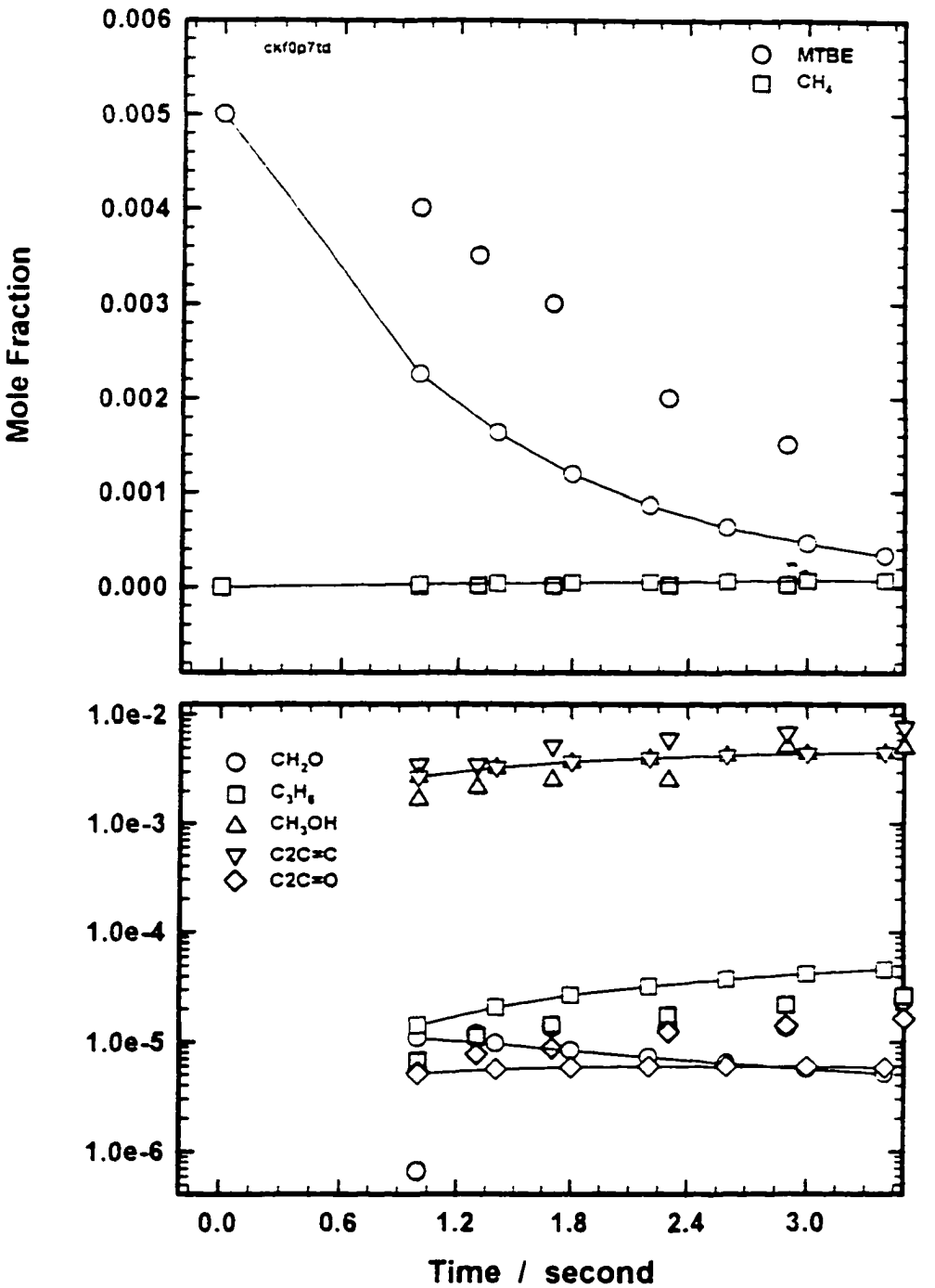
line is modeling result, symbols are experimental data

Figure IIC. 143 Comparison of experiment and modeling result
Pyrolysis, P = 4 atm, T = 873 K



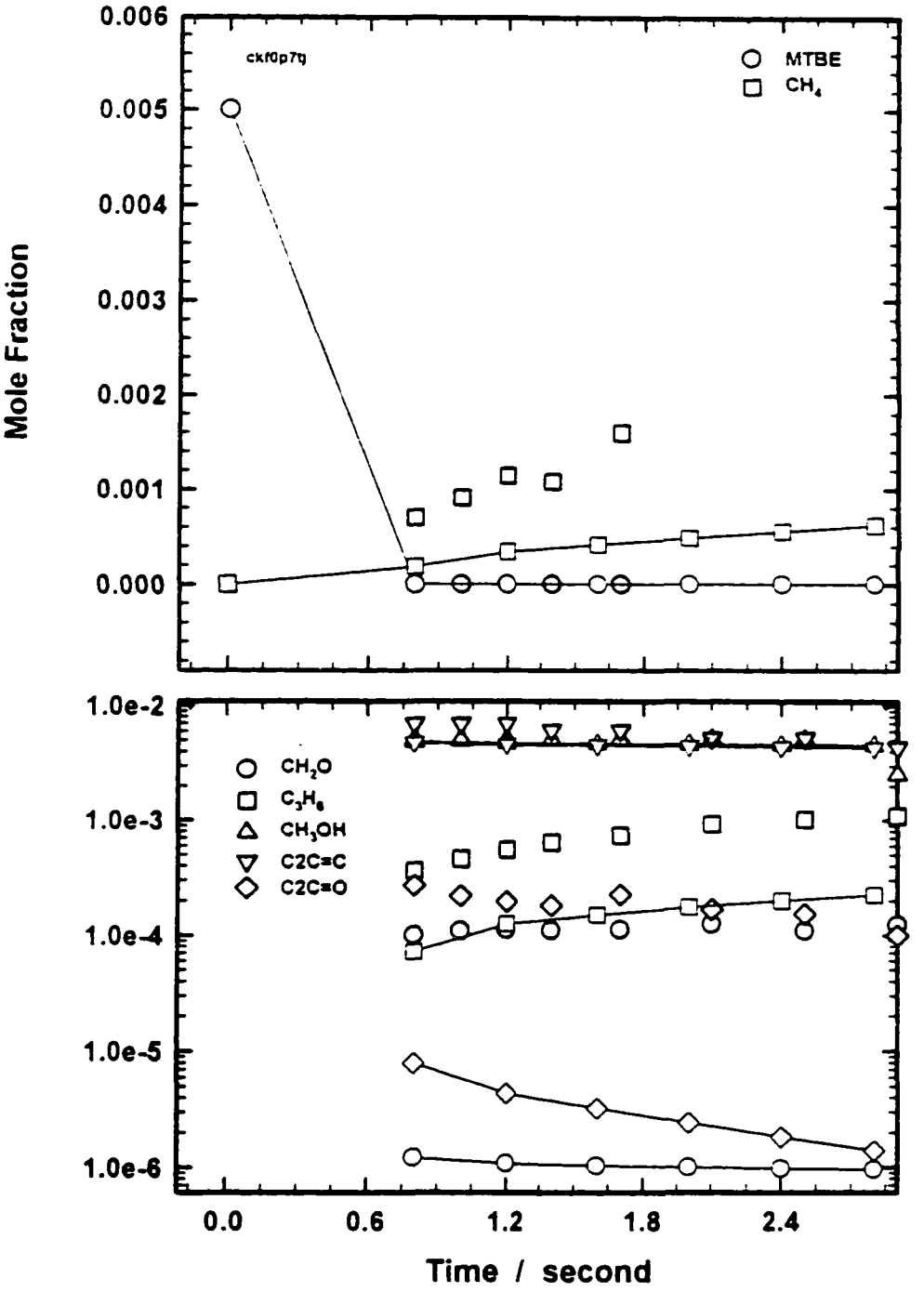
line is modeling result, symbols are experimental data

Figure IIC. 144 Comparison of experiment and modeling result
Pyrolysis, P = 4 atm, T = 1023 K



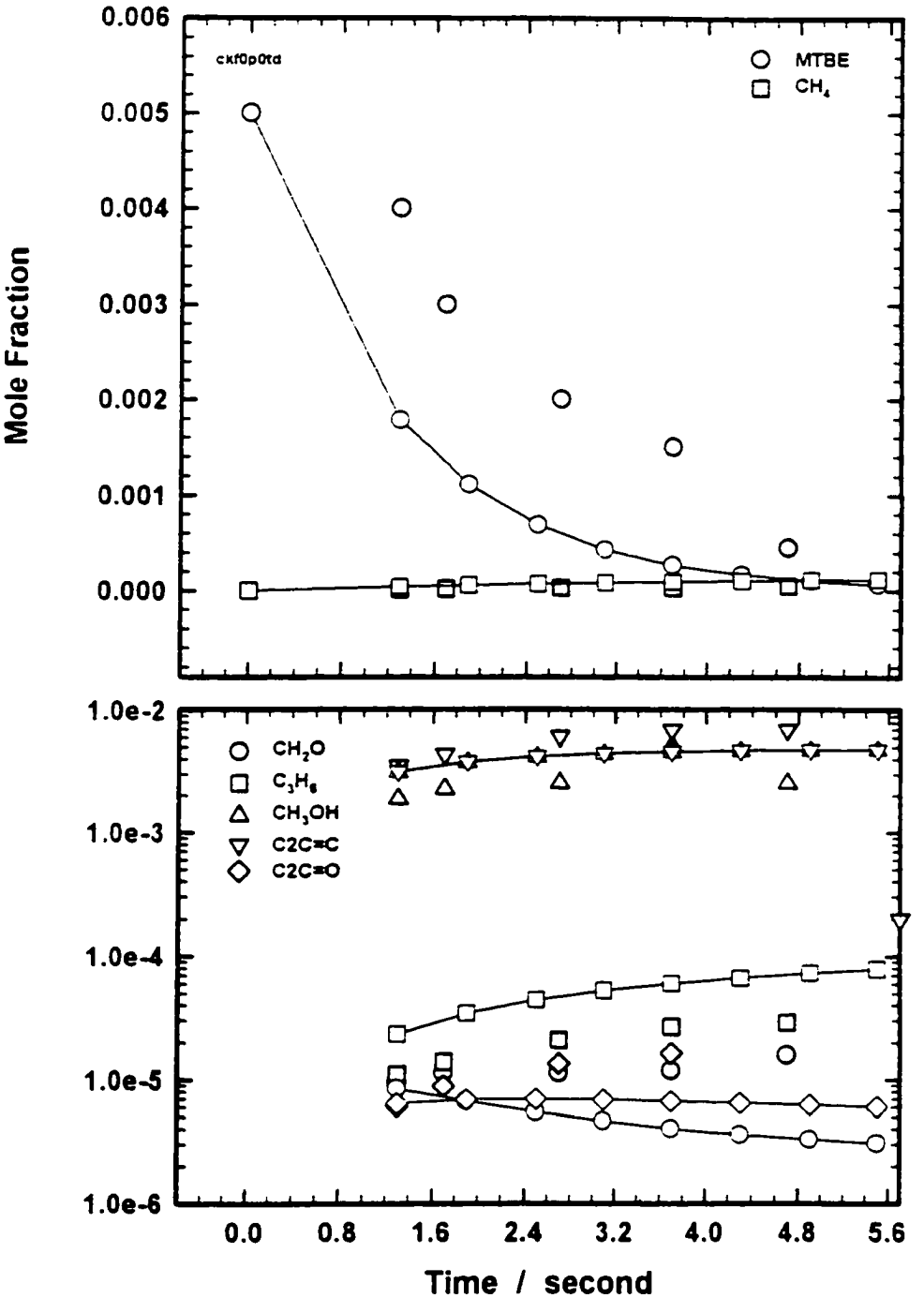
line is modeling result, symbols are experimental data

Figure IIC. 145 Comparison of experiment and modeling result
Pyrolysis, P = 7 atm, T = 873 K



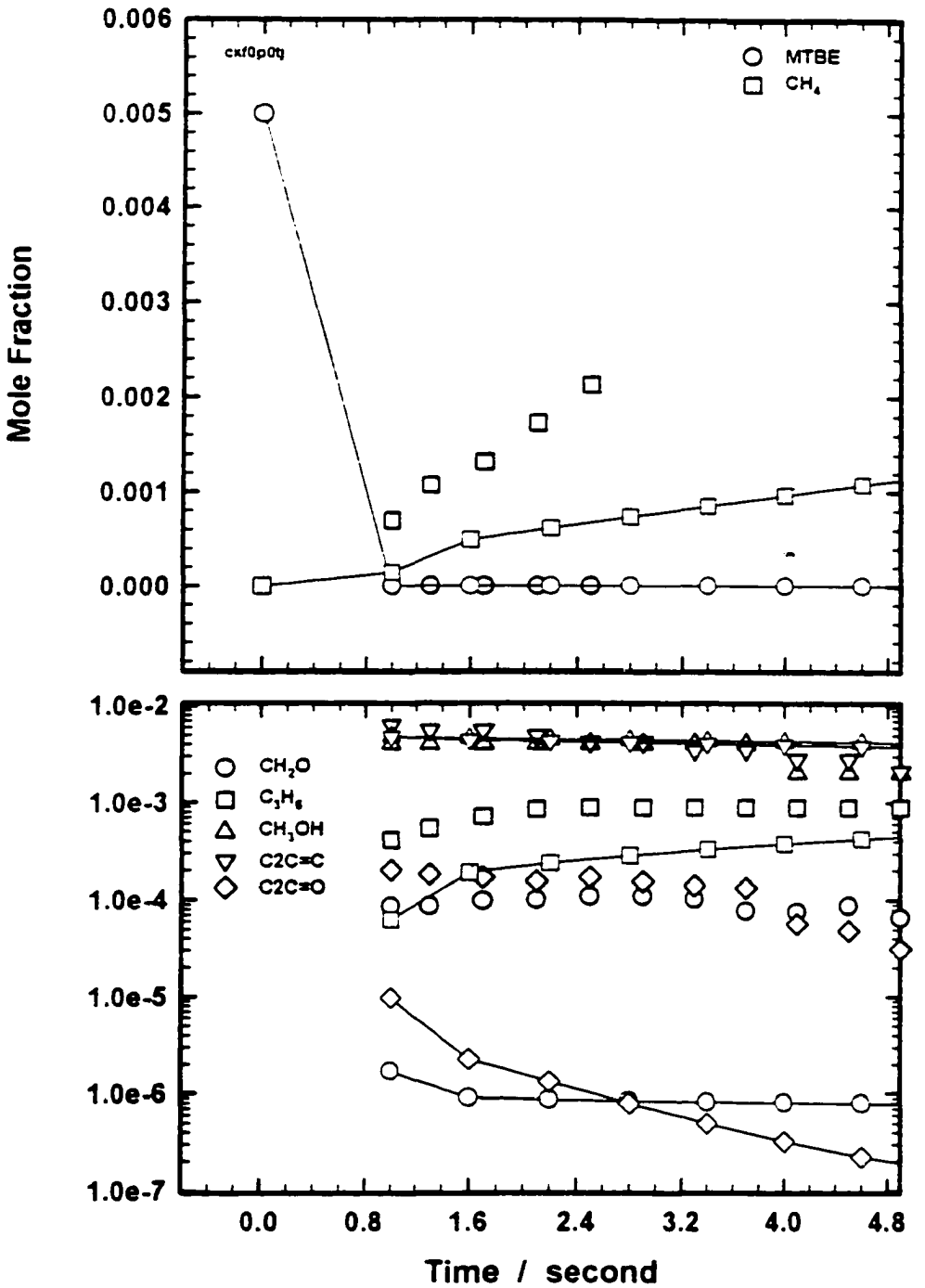
line is modeling result, symbols are experimental data

Figure IIC. 146 Comparison of experiment and modeling result
Pyrolysis, P = 7 atm, T = 1023 K



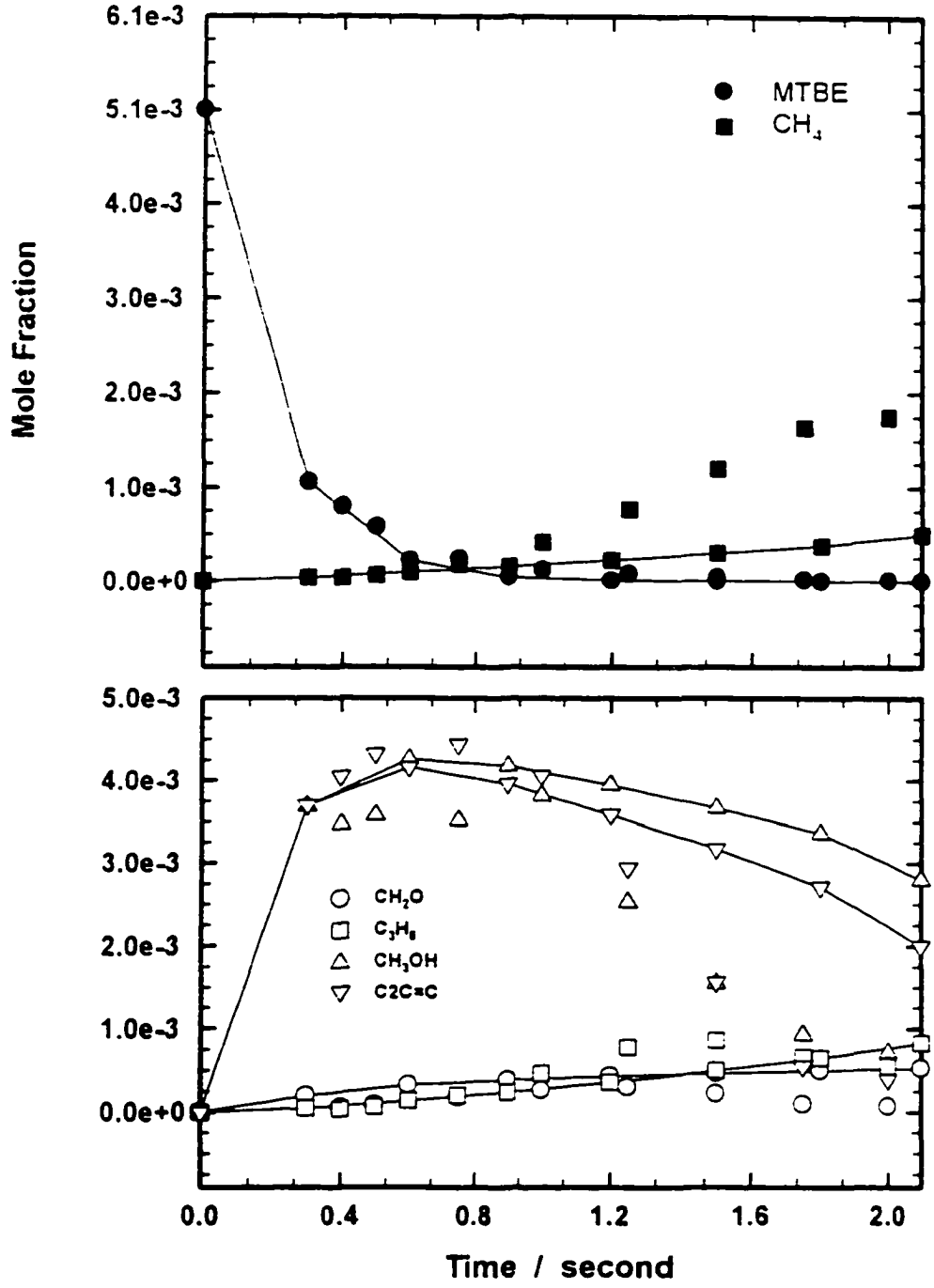
line is modeling result, symbols are experimental data

Figure IIC. 147 Comparison of experiment and modeling result
Pyrolysis, P = 10 atm, T = 873 K



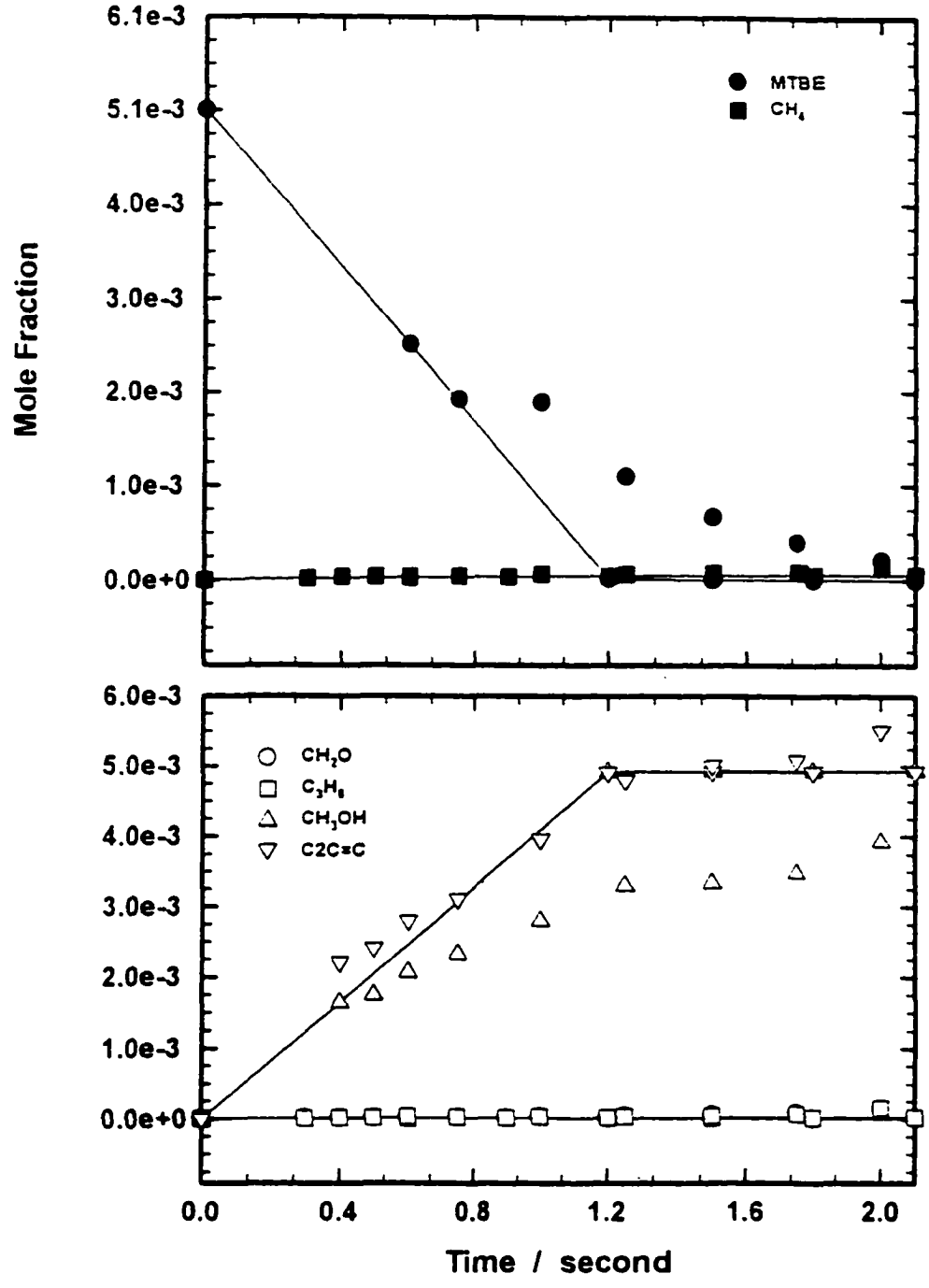
line is modeling result, symbols are experimental data

Figure IIC. 148 Comparison of experiment and modeling result
Pyrolysis, P = 10 atm, T = 1023 K



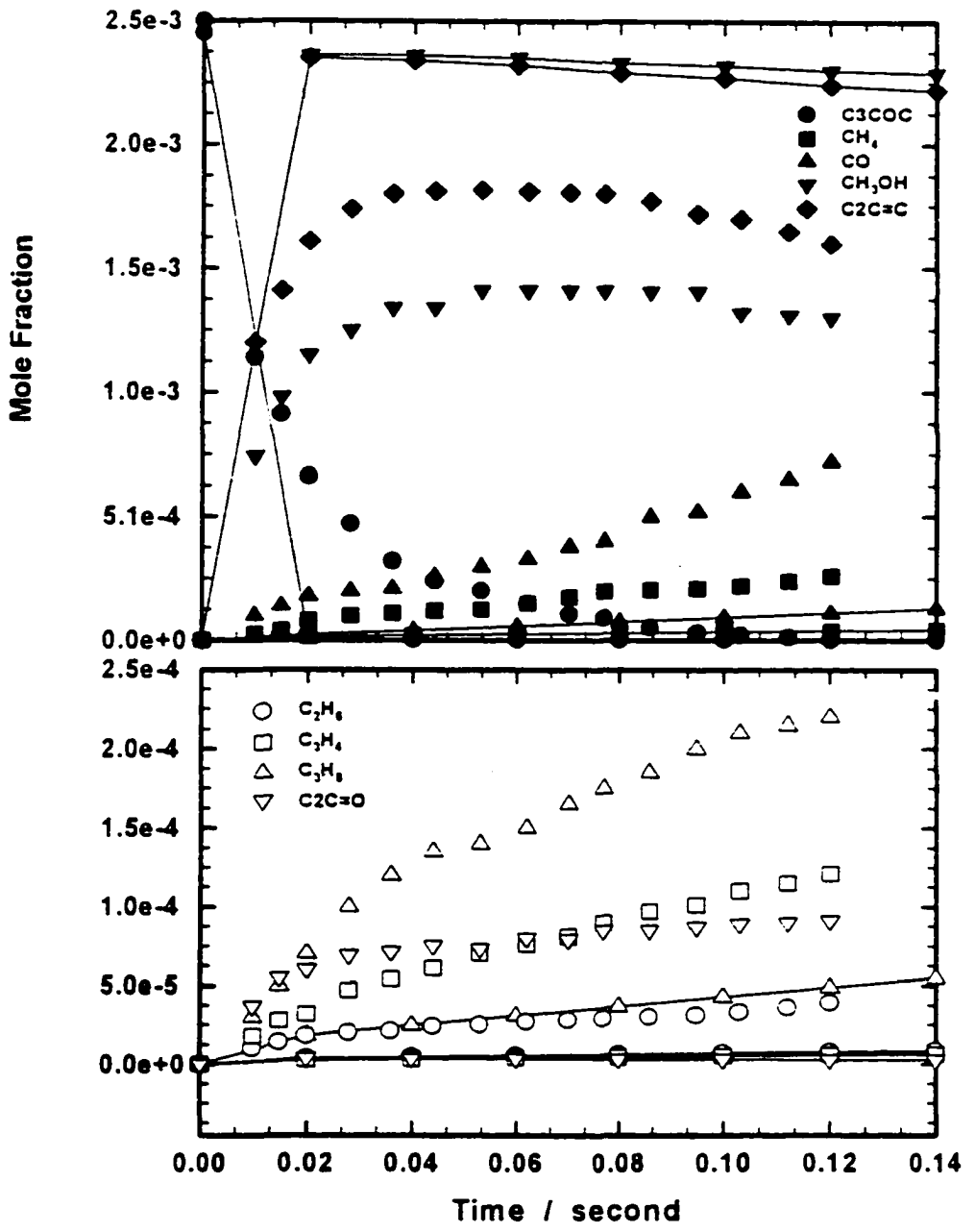
line is modeling result, symbols are experimental data

Figure IIC. 149 Comparison of experiment and modeling result
φ = 1.0, P = 1 atm, T = 923 K



line is modeling result, symbols are experimental data

Figure IIC. 150 Comparison of experiment and modeling result
Pyrolysis, P = 1 atm, T = 923 K



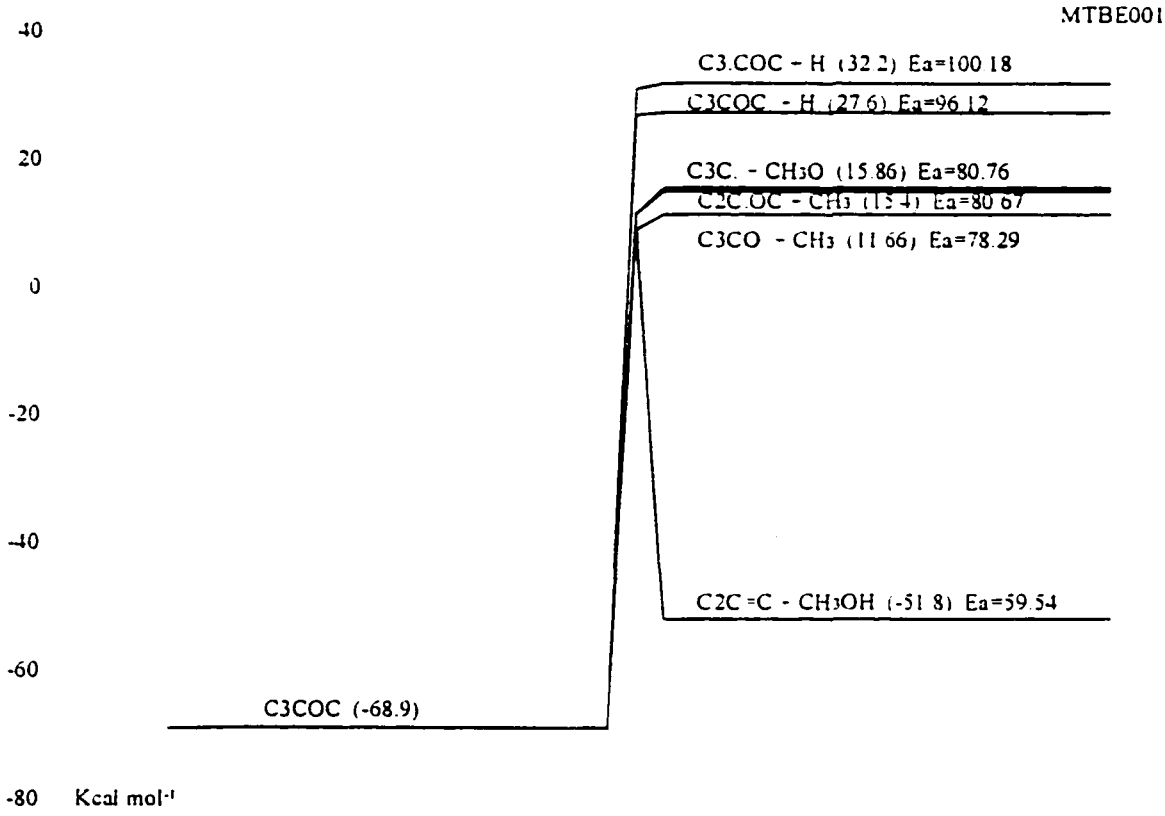
line is modeling result, symbols are experimental data

Figure IIC. 151 Comparison of experiment and modeling result
$\varphi = 0.96$, P = 1 atm, T = 1028 K

APPENDIX IID

QRRK INPUT PARAMETERS IN THE MTBE SYSTEM

IID. 1 MTBE → Products



	Reaction	A $T^n e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	C3COC → C2C=C + CH_3OH	$2.20\times10^{10}\ T^{1.22}\ e^{-0T}$	59.54
k_2	C3COC → C3C. + CH_3O	$5.99\times10^{16}\ T^{0}\ e^{-0T}$	80.76
k_3	C3COC → C3CO. + CH_3	$7.06\times10^{15}\ T^{0}\ e^{-0T}$	78.29
k_4	C3COC → C2C.OC + CH_3	$3.70\times10^{21}\ T^{-1.81}\ e^{-0.00143T}$	80.67
k_5	C3COC → C3.COC + H	$1.56\times10^{16}\ T^{0}\ e^{-0T}$	100.18
k_6	C3COC → C3COC. + H	$1.21\times10^{15}\ T^{0}\ e^{-0T}$	96.12

frequency/degeneracy (CPFIT)

C3COC: 559.6 (21.177); 1680.8 (17.127); 3331.4 (7.196)

Lennard-Jones parameter

σ(Å) = 5.5471, ε/k (K) = 584.86

k_1 A_f is from AFACT2f thermodynamic analysis with thermodynamic properties calculated by MOPAC PM3, $E_{a,f}$ from NIST fit

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.04 \times 10^{12}$, 90 TSA. $E_{a,f} = \Delta U_{rxn} = 80.76$ kcal mol^{-1}.

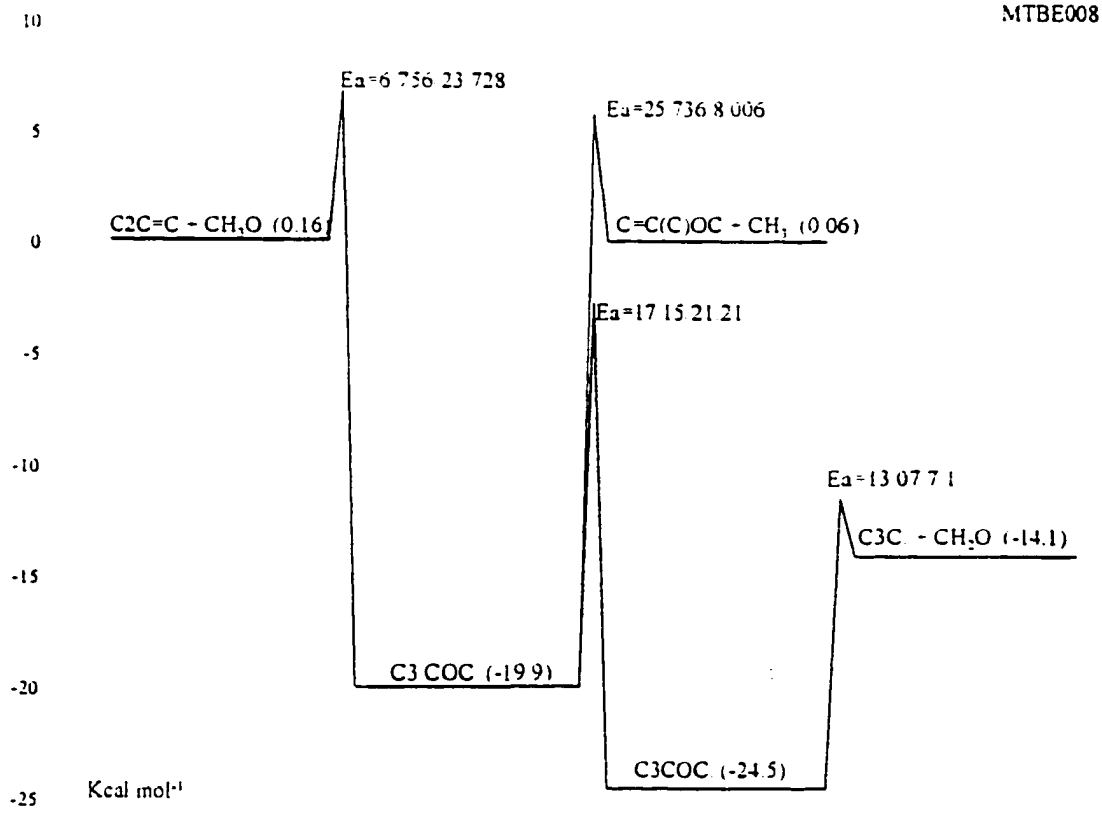
k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.21 \times 10^{13}$, 86 TSA/HAM for $CH_3O + CH_3 \rightarrow COC$. $E_{a,f} = \Delta U_{rxn} = 78.29$ kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.63 \times 10^{13} T^{-0.596}$, 90 TSA for C3C. + $CH_3 \rightarrow$ neo-C5. $E_{a,f} = \Delta U_{rxn} = 80.67$ kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.61 \times 10^{13}$, 90 TSA for C3C. + H $\rightarrow$ Prod.. $E_{a,f} = \Delta U_{rxn} = 100.18$ kcal mol^{-1}.

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.30 \times 10^{13}$, Bozzelli lecture note CCC. + H $\rightarrow$ CCC. $E_{a,f} = \Delta U_{rxn} = 96.12$ kcal mol^{-1}.

IID. 2 C3.COC/C3COC. → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C=C + CH_3O → C3.COC	1.21×10^{11} T^0 e^{-0T}	6.76
k_{-1}	C3.COC → C2C=C + CH_3O	1.90×10^{12} T^0 e^{-0T}	23.73
k_2	C3.COC → C=C(C)OC + CH_3	1.48×10^{13} T^0 e^{-0T}	25.74
k_3	C3.COC → C3COC.	1.44×10^{6} $T^{1.78}$ $e^{-0.00035T}$	17.15
k_{-3}	C3COC. → C3.COC	7.72×10^{8} $T^{1.0}$ e^{-0T}	21.21
k_4	C3COC. → C3C. + CH_2O	3.12×10^{12} T^0 e^{-0T}	13.07

frequency/degeneracy (CPFIT)
C3.COC: 560.0 (20.916); 1815.8 (16.374); 3598.5 (5.200)
C3COC.: 552.0 (21.562); 1791.0 (15.756); 3590.0 (5.182)
Lennard-Jones parameter
σ(Å) = 5.54, ε/k (K) = 584.86

k_1 taken from 86 TSA/HAM for CH_3O + C=C → Prod.

k_1 A_r via A_f and Microscopic Reversbility (MR) $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -16.97 kcal mol^{-1}

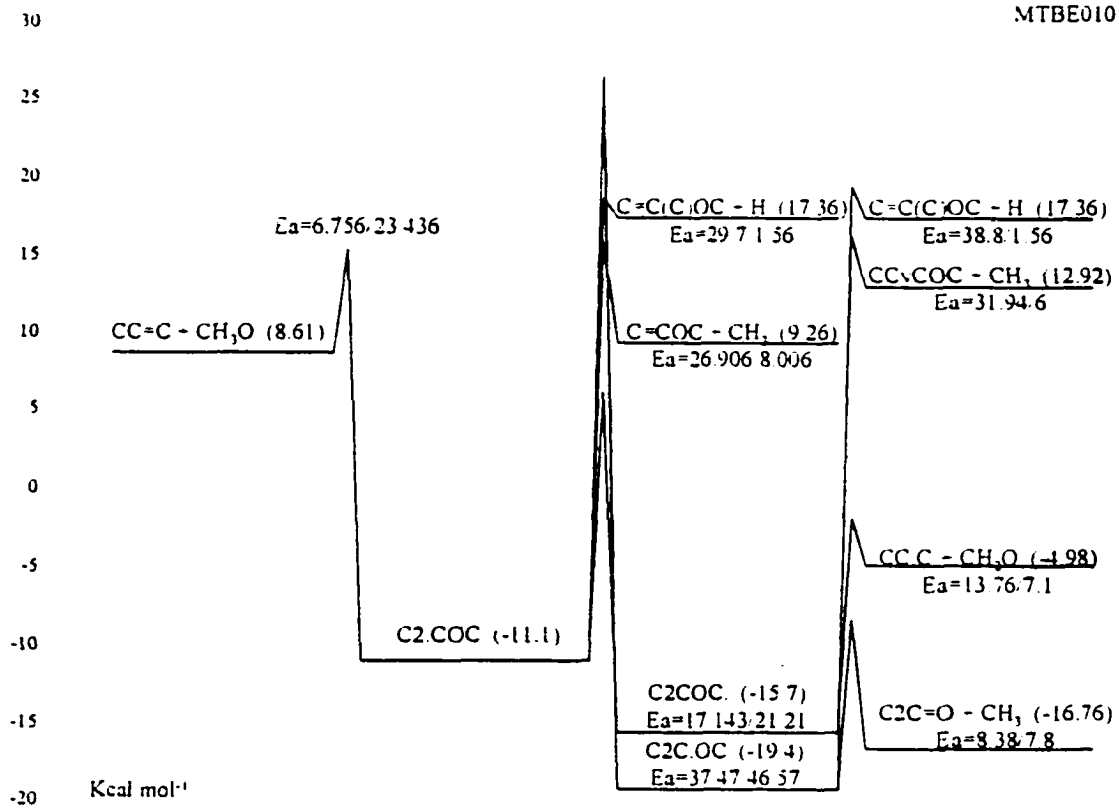
k_2 A_f via A_r and Microscopic Reversbility (MR), A_r = 9 64 × 10^{10}. 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 17.73 kcal mol^{-1}. $E_{a,r}$ = 8.006 kcal mol^{-1}. (referenced as the same as the A_r).

k_3 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 4.06 kcal mol^{-1}

k_{-3} A_r estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\ddagger}(T)/R$), deg. = 9, ek_b/h = 5 66 × 10^{10}, n = 1.0, $\Delta S^{\ddagger}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}). $E_{a,f}$ = RS (6) + E_{abst} (11.15) + ΔU_{rxn} (4.06) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), A_r = 2.82 × 10^{10}, 72 KER for C3C. + C=C $\rightarrow$ C3CCC.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 5.97 kcal mol^{-1}. $E_{a,r}$ = 7.10 kcal mol^{-1}. (referenced as the same as the A_r).

IID. 3 C2.COC → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC=C + CH_3O → C2.COC	1.21×10^{11} T^0 e^{-0T}	6.76
k_{-1}	C2.COC → CC=C + CH_3O	1.50×10^{12} T^0 e^{-0T}	23.36
k_2	C2.COC → C=C(C)OC + H	2.28×10^{12} T^0 e^{-0T}	31.05
k_3	C2.COC → C=COC + CH_3	3.42×10^{12} T^0 e^{-0T}	26.91
k_4	C2.COC → C2COC.	2.74×10^{6} $T^{1.79}$ $e^{-0.00037T}$	17.14
k_{-4}	C2COC. → C2.COC	5.15×10^{8} $T^{1.0}$ e^{-0T}	21.21
k_5	C2COC. → CCyCOC + CH_3	4.68×10^{11} T^0 e^{-0T}	31.94
k_6	C2COC. → CC.C + CH_2O	7.88×10^{11} T^0 e^{-0T}	13.76
k_7	C2.COC → C2C.OC	3.49×10^{12} $T^{-0.04}$ $e^{-0.0004T}$	37.47
k_{-7}	C2C.OC → C2.COC	3.90×10^{10} $T^{1.0}$ e^{-0T}	46.57
k_8	C2C.OC → C2C=O + CH_3	6.71×10^{12} T^0 e^{-0T}	8.38
k_9	C2C.OC → C=C(C)OC + H	2.92×10^{13} T^0 e^{-0T}	38.80

frequency/degeneracy (CPFIT)
C2.COC: 518.9 (14.066); 1404.9 (10.574); 2806.5 (9.36)

C2COC.. 525.2 (15.353); 1474.1 (10.557); 2908.5 (8.09)
C2C.OC 516.8 (13.691); 1614.9 (12.169), 2927.8 (8.141)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 taken from 86 TSA/HAM for CH_3O + C=C → Prod.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-16.60) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 7.23 \times 10^{12} = 1/2$ (H + CC=C → CCC.), 91 TSA/HAM, $E_{a,f} = E_{a,r}$ (2.906) + ΔU_{rxn} (28.14) kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + CH_3 → C3.C. $E_{a,f} = E_{a,r}$ (8.006) + ΔU_{rxn} (18.90) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (4.07) kcal mol^{-1}.

k_{-4} A_r estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}$(T)/R), deg. = 6, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}$(T) is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}). $E_{a,f}$ = RS (6) + E_{abst} (11.14) + ΔH_{rxn} (4.07) kcal mol^{-1}.

k_5 A_f estimated using TST, A = (deg.) (ek_bT/h) exp($\Delta S^{\neq}$(T)/R), deg. = 1, ek_bT/h = $10^{13.55}$?, $\Delta S^{\neq}$(T) is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (25.94) kcal mol^{-1}. $E_{a,r}$ = 6.0 kcal mol^{-1} (estimated by Bozzelli).

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.82 \times 10^{10}$, 72 KER for C3C. + C=C → C3CCC.. $E_{a,f} = E_{a,r}$ (7.10) + ΔU_{rxn} (6.66) kcal mol^{-1}.

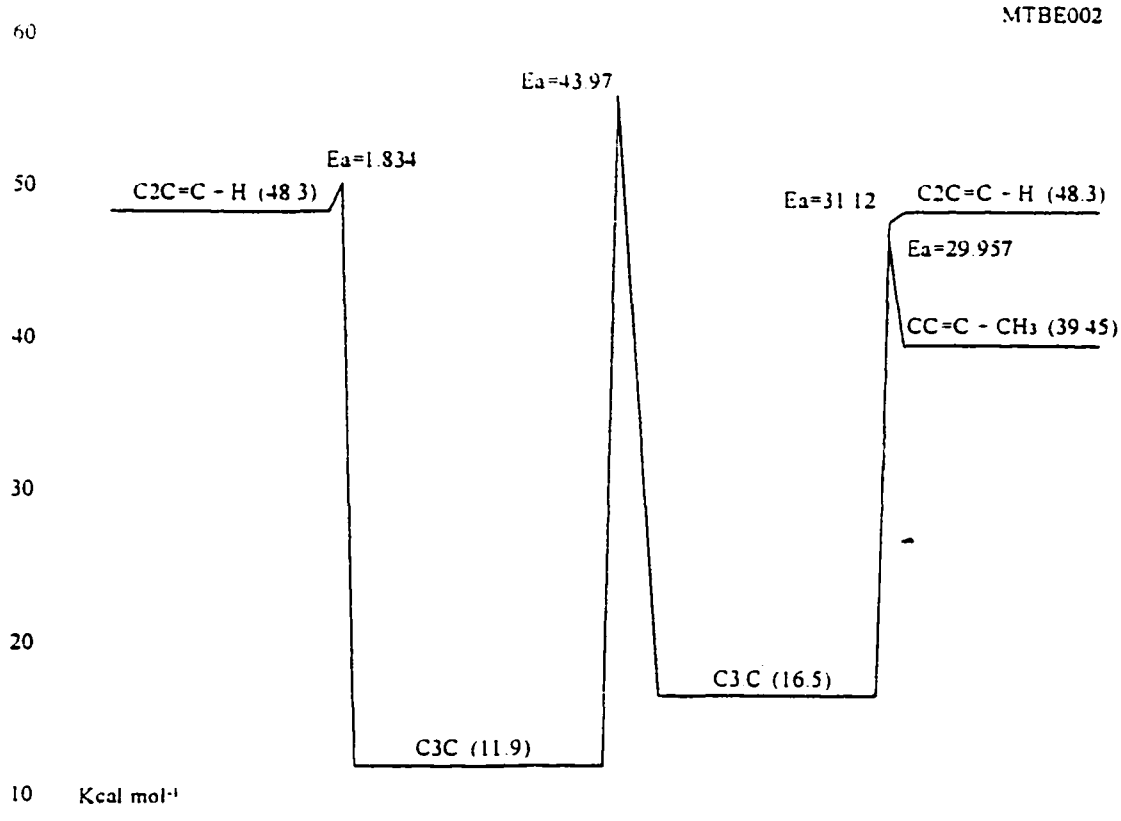
k_7 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (9.10) kcal mol^{-1}.

k_{-7} A_r estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}$(T)/R), deg. = 6, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}$(T) is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f}$ = RS (28) + E_{abst} (9.47) + ΔH_{rxn} (9.10) kcal mol^{-1}.

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.69 \times 10^{11}$, 91 TSA for CH_3 + CC=C → CC.CC. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (0.58) kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_9 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12} = 1/2$ (H + CC=C → CC.C), 91 TSA/HAM. $E_{a,f} = E_{a,r}$ (1.56) + ΔU_{rxn} (37.24) kcal mol^{-1}.

IID. 4 C3C./C3.C → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C=C + H → C3C.	6.15×10^{9} $T^{1.33}$ e^{-0T}	2.33
k_{-1}	C3C. → C2C=C + H	2.01×10^{11} $T^{0.58}$ $e^{-0.00008T}$	38.15
k_2	C3C. → C3.C	5.85×10^{10} $T^{1.0}$ e^{-0T}	43.97
k_{-2}	C3.C → C3C.	1.70×10^{12} $T^{0.21}$ $e^{-0.00029T}$	38.77
k_3	C3.C → CC=C + CH_3	2.00×10^{13} T^{0} e^{-0T}	29.98
k_4	C3.C → C2C=C + H	2.86×10^{10} T^{0} e^{-0T}	31.12

frequency/degeneracy (CPFIT)
C3C.: 250.0 (6.593); 1226.0 (14.014); 2721.0 (10.893)
C3.C: 250.0 (5.631); 1074.1 (14.902); 2708.2 (10.968)
Lennard-Jones parameter
σ(Å) = 5.18, ε/k (K) = 357.0

k_1 A_f from AFACT2f thermodynamic analysis with thermodynamic properties from

chiungchu, $E_{a,f}$ from 90 TSA.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (35.82) kcal mol^{-1}.

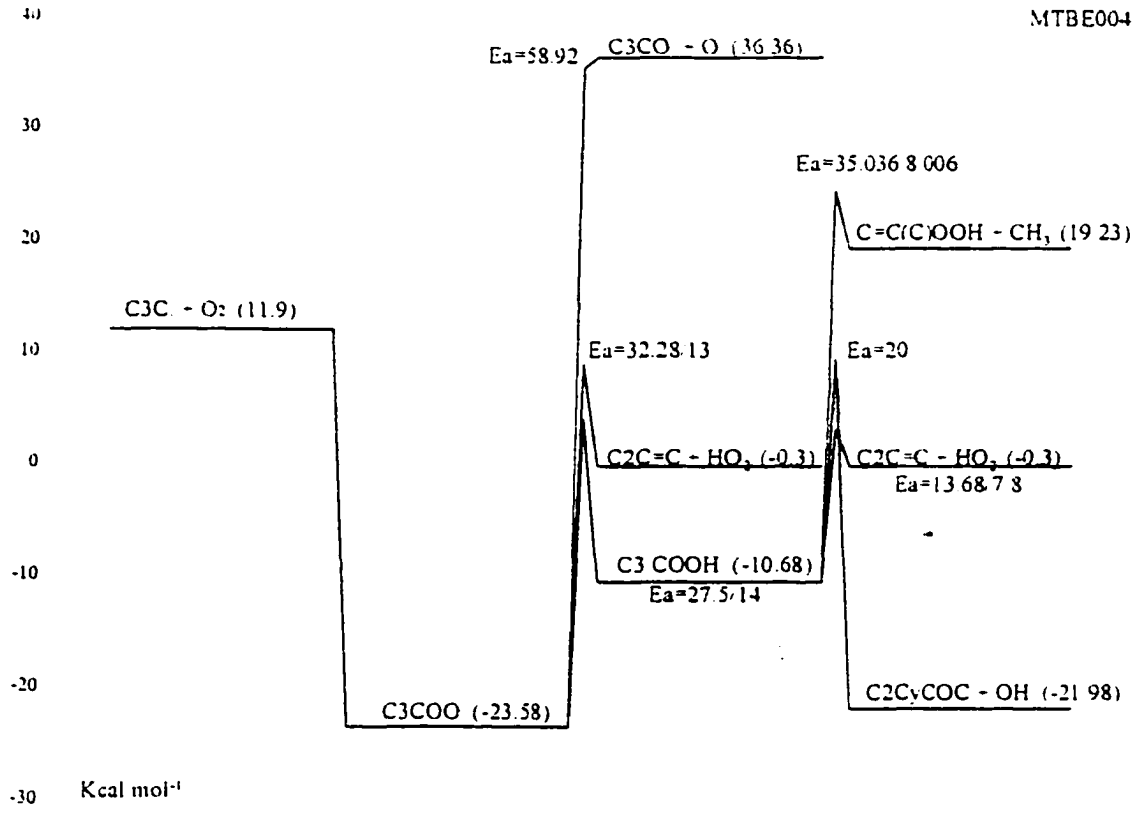
k_2 A_f estimated using TST, A = (deg.) (ek_b/h) $\exp(\Delta S^{\neq}(T)/R)$ T^n, deg. = 9, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f} = RS$ (28) + E_{abst} (10.77) + ΔH_{rxn} (5.2) kcal mol^{-1}.

k_{-2} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 5.2 kcal mol^{-1}

k_3 90 TSA

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.26 \times 10^{11}$ T^0, 72 KER. $E_{a,f} = \Delta U_{rxn}$ = 31.12 kcal mol^{-1}.

IID. 5 C3C. + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C3C. + O_2 → C3COO.	1.81×10^{12} T^0 e^{-0T}	0.00
k_{-1}	C3COO. → C3C. + O_2	2.03×10^{15} T^0 e^{-0T}	32.26
k_2	C3COO. → C3CO. + O	5.82×10^{15} T^0 e^{-0T}	58.92
k_3	C3COO. → C2C=C + HO_2	2.59×10^{11} $T^{1.22}$ e^{-0T}	32.28
k_4	C3COO. → C3.COOH	6.77×10^{10} $T^{1.22}$ e^{-0T}	27.50
k_{-4}	C3.COOH → C3COO.	1.10×10^{12} $T^{-0.09}$ $e^{-0.00087T}$	14.00
k_5	C3.COOH → C2CyCOC + OH	1.38×10^{12} $T^{-0.03}$ e^{-0T}	20.00
k_6	C3.COOH → C2C=C + HO_2	1.06×10^{13} $T^{-0.03}$ e^{-0T}	13.68
k_7	C3.COOH → C=C(C)OOH + CH_3	4.33×10^{13} T^0 e^{-0T}	35.04

frequency/degeneracy (CPFIT)
C3COO.: 250.4 (9.685); 1072.1 (16.487); 2880.5 (10.829)
C3.COOH: 251.5 (10.679); 1084.5 (16.339); 2872.0 (9.482)
Lennard-Jones parameter
σ(Å) = 5.54, ε/k (K) = 584.86.0

k_1 92 WAL/AND, for C3C. + O_2.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 32.26 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for $O + CH_3O \rightarrow$ Prod.. $E_{a,f} = \Delta U_{rxn}$ = 58.92 kcal mol^{-1}

k_3 A_f estimated using TST, A = (deg.) $A' T^n$, deg. = 9, $A' = 2.876 \times 10^{10}$, n = 1.22, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r}$, + ΔU_{rxn}, $E_{a,r}$ is estimated as 13 kcal mol^{-1} in this study, ΔU_{rxn} = 19.38 kcal mol^{-1}.

k_4 A_f estimated using TST, A = (deg.) $A' T^n$, deg. = 6, $A' = 3.836 \times 10^9$, n = 1.071, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (6) + E_{abs} (8.0) + ΔH_{rxn} (13.50) kcal mol^{-1}.

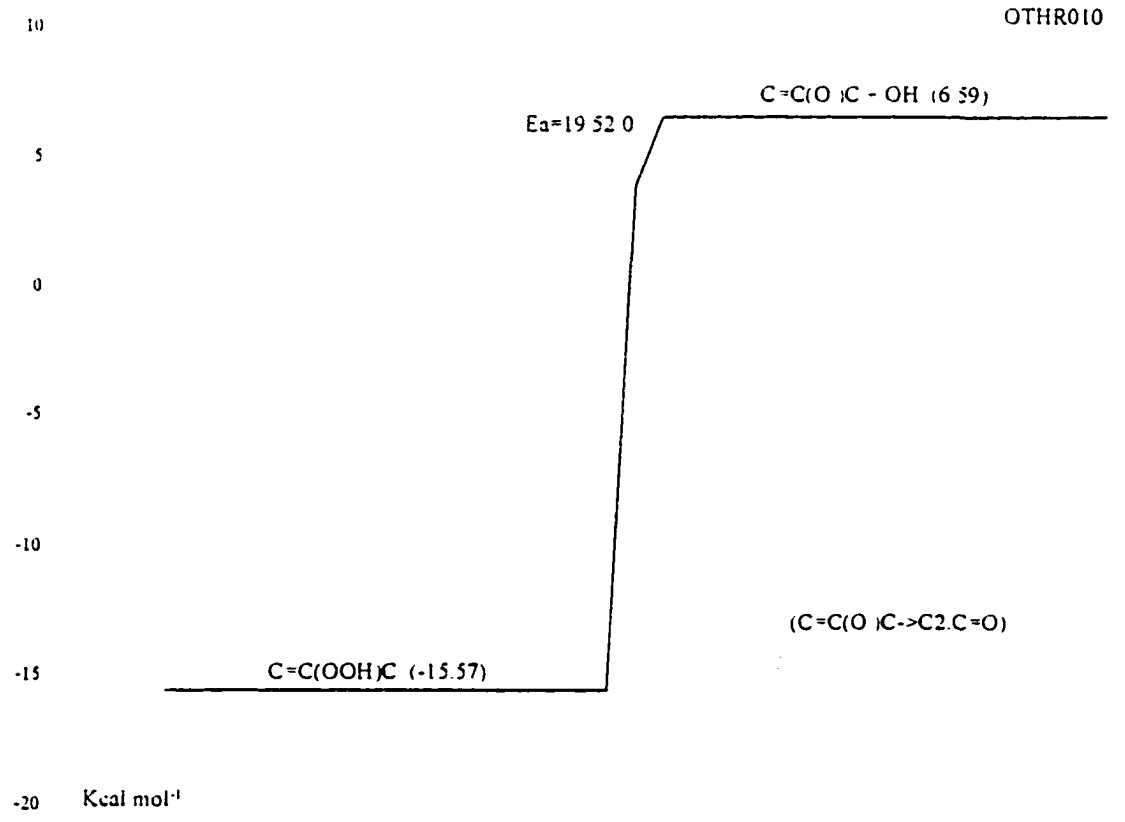
k_{-4} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 13.50 kcal mol^{-1}.

k_5 A_f estimated using TST, A = (deg.) $A' T^n$, deg. = 1, $A' = 1.384 \times 10^{12}$, n = -0.031, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r}$ + ΔU_{rxn}, $E_{a,r}$ is estimated in this study.

k_6 A_f estimated using TST, A = (deg.) $A' T^n$, deg. = 1, $A' = 1.063 \times 10^{13}$, n = -0.027, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r}$ + ΔU_{rxn}, $E_{a,r}$ = 7.8 kcal mol^{-1}. (Bozzelli), ΔU_{rxn} = 5.88 kcal mol^{-1}.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 35.036 kcal mol^{-1}. $E_{a,r}$ = 8.006 kcal mol^{-1}. (referenced as the same as the A_r).

IID. 6 C=C(OOH)C → C2.C=O (C=C(O.)C) + OH

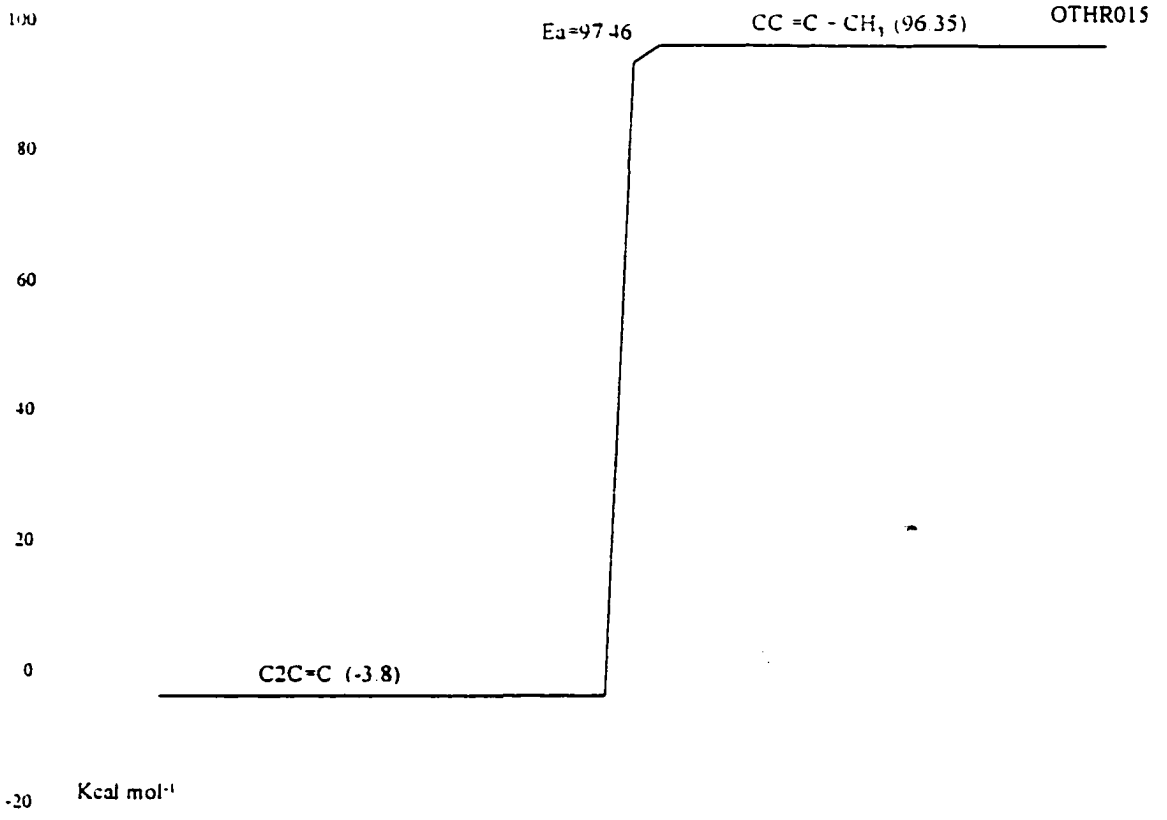


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C=C(OOH)C → (C=C(O.)C) + OH	5.98×10^{14} T^0 e^{-0T}	19.52

frequency/degeneracy (CPFIT)
C=C(OOH)C: 526.0 (12.851); 1827.0 (10.334); 4000.0 (2.315)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 91 TSA for C=CC. + OH). $E_{a,f} = \Delta U_{rxn} = 19.52$ kcal mol^{-1}.

IID. 7 C2C=C → CC.=C + CH_3

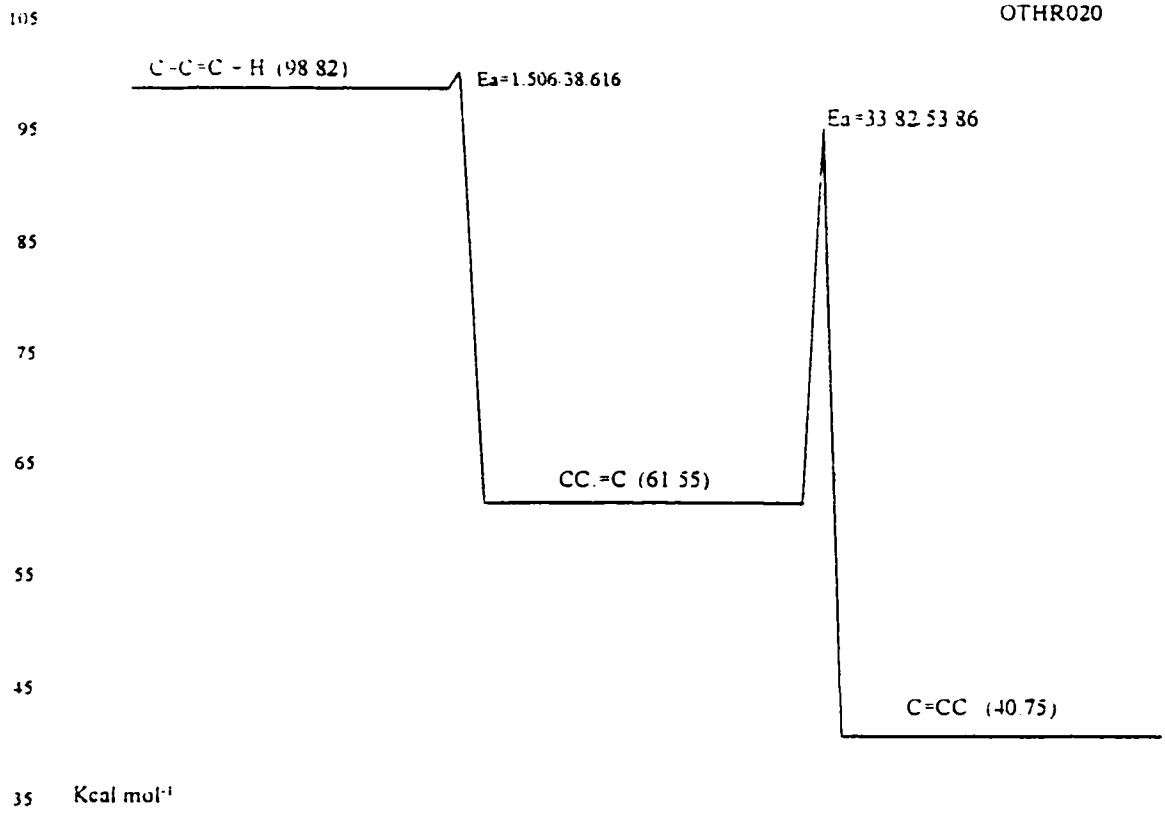


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	C2C=C → CC.=C + CH_3	1.93×10^{17} T^0 e^{-0T}	97.46

frequency/degeneracy (CPFIT)
C2C=C: 435.4 (8.508); 1327.6 (12.429); 2967.5 (8.063)
Lennard-Jones parameter
σ(Å) = 5.18, ε/k (K) = 407.0

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.61 \times 10^{13}$, 92 BAU/COB for $CH_3 + CH_3 \rightarrow C_2H_6$. $E_{a,f} = \Delta U_{rxn} = 97.46$ kcal mol^{-1}.

IID. 8 CC.=C → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C=C=C + H → CC.=C	1.00×10^{13} T^0 e^{-0T}	1.506
k_{-1}	CC.=C → C=C=C + H	4.46×10^{12} T^0 e^{-0T}	38.62
k_2	CC.=C → C=CC.	1.95×10^{10} $T^{1.0}$ e^{-0T}	33.82

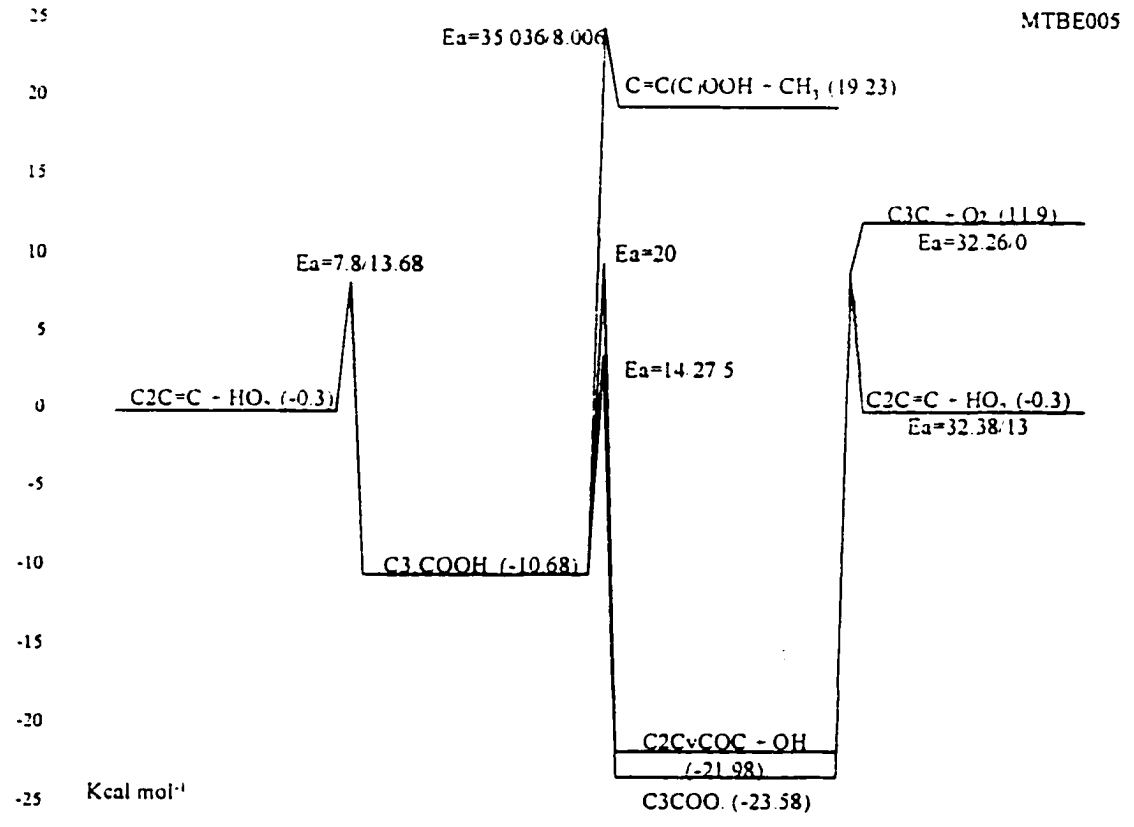
frequency/degeneracy (CPFIT)
C=C.C: 473.2 (4.836); 1413.1 (7.638); 3019.1 (5.025)
Lennard-Jones parameter
σ(Å) = 4.57, ε/k (K) = 307.60

k_1 $A_f = 1.00 \times 10^{13}$, 84 WAR for C=C + H. $E_{a,f} = 1.506$ kcal mol^{-1} taken from the same reference.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, $\Delta U_{rxn} = -37.11$ kcal mol^{-1}.

k_2 A_r estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 3, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f}$ = RS (28) + E_{abst} (13.82) kcal mol^{-1}.

IID. 9 C2C=C + HO_2 → [C3.COOH]* → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C=C + HO_2 → C3.COOH	7.43×10^{0} $T^{3.87}$ $e^{0.00068T}$	7.80
k_{-1}	C3.COOH → C2C=C + HO_2	1.06×10^{13} $T^{-0.03}$ e^{-0T}	13.68
k_2	C3.COOH → C2CyCOC + OH	1.38×10^{12} $T^{-0.03}$ e^{-0T}	20.00
k_3	C3.COOH → C=C(C)OOH + CH_3	4.33×10^{13} T^{0} e^{-0T}	35.04
k_4	C3.COOH → C3COO.	1.10×10^{12} $T^{-0.09}$ $e^{-0.00087T}$	14.00
k_{-4}	C3COO. → C3.COOH	6.77×10^{10} $T^{1.22}$ e^{-0T}	27.50
k_5	C3COO. → C2C=C + HO_2	2.59×10^{11} $T^{1.22}$ e^{-0T}	32.28
k_6	C3COO. → C3C. + O_2	2.03×10^{15} T^{0} e^{-0T}	32.26

frequency/degeneracy (CPFIT)
C3.COOH: 251.5 (10.679); 1084.5 (16.339); 2872.0 (9.482)
C3COO.: 250.4 (9.685); 1072.1 (16.487); 2880.5 (10.829)
Lennard-Jones parameter
σ(Å) = 5.54, ε/k (K) = 584.86.0

k_1 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = 7.8$ kcal mol^{-1} (Bozzelli).

k_{-1} A_r estimated using TST, A = (deg.) A′ T^n, deg. = 1, A′ = 1.063×10^{13}, n = -0.027, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,r}$ via $E_{a,f}$, - ΔU_{rxn}, $E_{a,f} = 7.8$ kcal mol^{-1}. (Bozzelli), $\Delta U_{rxn} = 5.88$ kcal mol^{-1}.

k_2 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 1, A′ = 1.384×10^{12}, n = -0.031, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r} + \Delta U_{rxn}$, $E_{a,r}$ is estimated in this study.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for $C_3H_6 + CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 35.036$ kcal mol^{-1}. $E_{a,r} = 8.006$ kcal mol^{-1}. (referenced as the same as the A_r).

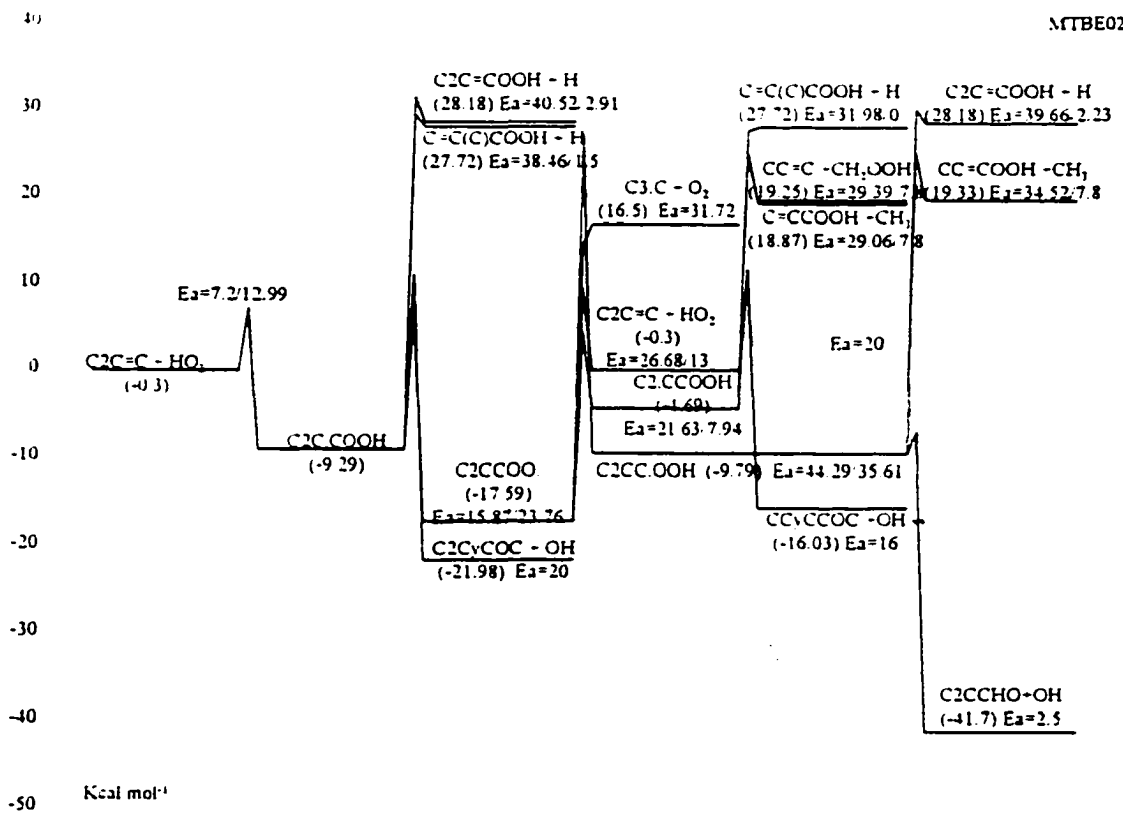
k_4 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} - \Delta U_{rxn}$, $\Delta U_{rxn} = 13.50$ kcal mol^{-1}.

k_{-4} A_r estimated using TST, A = (deg.) A′ T^n, deg. = 6, A′ = 3.836×10^9, n = 1.071, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,r}$ = RS (6) + E_{abst} (8.0) + ΔH_{rxn} (13.50) kcal mol^{-1}.

k_5 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 9, A′ = 2.876×10^{10}, n = 1.22, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r} + \Delta U_{rxn}$, $E_{a,r}$ is estimated as 13 kcal mol^{-1} in this study, $\Delta U_{rxn} = 19.38$ kcal mol^{-1}.

k_6 A_r via A_f and Microscopic Reversbility (MR), $A_f = 1.81 \times 10^{12}$, 92 WAL/AND, for C3C. + O_2), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 32.26$ kcal mol^{-1}.

IID. 10 C2C=C + HO_2 → [C2C.COOH]* → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C=C + HO_2 → C2C.COOH	6.39×10^{2} $T^{3.10}$ e^{-0T}	7.20
k_{-1}	C2C.COOH → C2C=C + HO_2	1.54×10^{9} $T^{1.07}$ $e^{-0.00016T}$	12.99
k_2	C2C.COOH → C2CyCOC + OH	3.00×10^{8} $T^{1.06}$ e^{-0T}	20.00
k_3	C2C.COOH → C=C(C)COOH + H	3.02×10^{13} T^{0} e^{-0T}	38.46
k_4	C2C.COOH → C2C=COOH + H	9.14×10^{11} T^{0} e^{-0T}	40.52
k_5	C2C.COOH → C2CCOO.	3.31×10^{5} $T^{1.79}$ e^{-0T}	15.87
k_{-5}	C2CCOO. → C2C.COOH	4.42×10^{7} $T^{1.69}$ $e^{-0.00028T}$	23.76
k_6	C2CCOO. → C2C=C + HO_2	7.47×10^{9} $T^{0.74}$ e^{-0T}	26.68
k_7	C2CCOO. → C3.C + O_2	2.30×10^{14} T^{0} e^{-0T}	31.72
k_8	C2CCOO. → C2.CCOOH	4.32×10^{8} $T^{1.32}$ e^{-0T}	21.63
k_{-8}	C2.CCOOH → C2CCOO.	1.17×10^{11} $T^{-0.33}$ $e^{-0.00107T}$	7.94
k_9	C2.CCOOH → C=CCOOH + CH_3	6.32×10^{12} T^{0} e^{-0T}	29.06
k_{10}	C2.CCOOH → CC=C + CH_2OOH	2.78×10^{13} T^{0} e^{-0T}	29.39
k_{11}	C2.CCOOH → CCyCCOC + OH	5.38×10^{10} T^{0} e^{-0T}	16.00
k_{12}	C2.CCOOH → C=C(C)COOH + H	8.62×10^{10} T^{0} e^{-0T}	31.98

	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_{13}	C2CCOO. → C2CC.OOH	2.60×10^{10} $T^{1.0}$ e^{-0T}	44.29
k_{-13}	C2CC.OOH → C2CCOO.	9.11×10^{12} $T^{-0.38}$ $e^{-0.00071T}$	35.61
k_{14}	C2CC.OOH → C2CCHO + OH	1.34×10^{15} T^{0} e^{-0T}	2.50
k_{15}	C2CC.OOH → C2C=COOH + H	9.30×10^{11} T^{0} e^{-0T}	39.66
k_{16}	C2CC.OOH → CC=COOH + CH_3	4.73×10^{12} T^{0} e^{-0T}	34.52

frequency/degeneracy (CPFIT)
C2C.COOH: 250.0 (11.309); 1364.5 (17.843); 2818.8 (7.349)
C2CCOO.: 250.2 (9.560); 1119.2 (16.494); 2788.5 (10.946)
C2.CCOOH: 250.0 (10.534); 1133.0 (16.419); 2777.2 (9.548)
C2CC.OOH: 250.2 (11.370); 1195.7 (16.616); 2826.5 (8.513)
Lennard-Jones parameter
σ(Å) = 5.54, ε/k (K) = 584.86.0

k_1 A_f, estimated using TST, A = (deg.) A′ T^n, deg. = 1, A′ = 6.39×10^2, n = 3.102, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = 7.2 kcal mol^{-1} (Bozzelli).

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 5.79 kcal mol^{-1}.

k_2 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 1, A′ = 2.996×10^8, n = 1.061, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ is estimated in this study.

k_3 A_f via A_r and Microscopic Reversbility (MR), A_r = 3.09×10^{13}, 72 KER for C2C=C + H → C3C.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 36.96 kcal mol^{-1}. $E_{a,r}$ = 1.50 kcal mol^{-1}. (referenced as the same as the A_r).

k_4 A_f via A_r and Microscopic Reversbility (MR), A_r = 3.615×10^{12} = 1/2(C_3H_6 + H → CCC.), 91 TSA. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 37.61 kcal mol^{-1}. $E_{a,r}$ = 2.906 kcal mol^{-1}. (referenced as the same as the A_r).

k_5 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 1, A′ = 3.314×10^5, n = 1.792, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = -7.89 kcal mol^{-1}.

k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r}$ = RS (6) + E_{abst} (9.87) + ΔH_{rxn} (7.89) kcal mol^{-1}.

k_6 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 1, A′ = 7.467×10^9, n = 0.735, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r} + \Delta U_{rxn}$, $E_{a,r}$ is estimated as

13 kcal mol^{-1} in this study, ΔU_{rxn} = 13.68 kcal mol^{-1}.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.0 \times 10^{12}$, 88 XI for C3CC. + $O_2 \rightarrow$ C3CCOO.. $E_{a,f} = \Delta U_{rxn}$, = 31.72 kcal mol^{-1}

k_8 A_f estimated using TST, A = (deg.) A' T^n, deg. = 6, A' = 7.202×10^7, n = 1.317, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (0) + E_{abst} (7.94) + ΔH_{rxn} (13.69) kcal mol^{-1}.

k_{-8} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 13.69 kcal mol^{-1}.

k_9 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 21.26 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_{10} A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 21.59 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_{11} A_f estimated using TST, A = (deg.) (ek_bT/h) exp($\Delta S^{\neq}(T)/R$), deg. = 1, ek_bT/h = $10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_{12} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.26 \times 10^{11}$, 72 KER. $E_{a,f}$ = ΔU_{rxn} = 31.98 kcal mol^{-1}.

k_{13} A_f estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}(T)/R$), deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (9.61) + ΔH_{rxn} (8.68) kcal mol^{-1}.

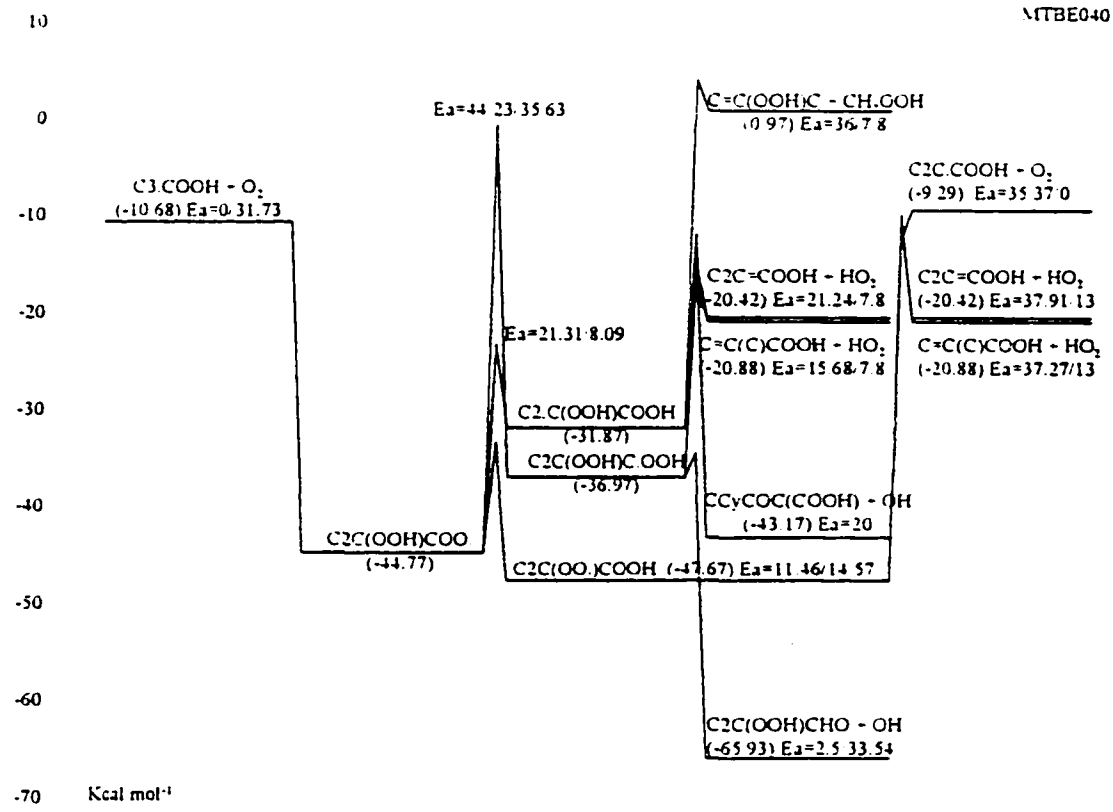
k_{-13} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 8.68 kcal mol^{-1}.

k_{14} A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O$ + OH (1990 Page)

k_{15} A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.215 \times 10^{12}$ = 1/4 (H + CC=C $\rightarrow$ CC.C), 91 TSA. $E_{a,f}$ is estimated as the average of terminal and non-terminal addition of H to carbon double bond of CC=C, 1/2 (1.506 + 2.906), 91 TSA.

k_{16} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.69 \times 10^{11}$, 91 TSA for CH_3 + CC=C $\rightarrow$ CC.CC. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 26.72 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

IID. 11 C3.COOH + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C3.COOH + O_2 → C2C(OOH)COO.	1.00×10^{12} T^0 e^{-0T}	0.00
k_{-1}	C2C(OOH)COO. → C3.COOH + O_2	2.31×10^{14} T^0 e^{-0T}	31.73
k_2	C2C(OOH)COO. → C2C(OOH)C.OOH	6.11×10^{9} $T^{1.0}$ e^{-0T}	44.23
k_{-2}	C2C(OOH)C.OOH → C2C(OOH)COO.	1.59×10^{12} $T^{-0.33}$ $e^{-0.00073T}$	35.63
k_3	C2C(OOH)C.OOH → C2C(OOH)CHO + OH	3.22×10^{13} T^0 e^{-0T}	2.50
k_4	C2C(OOH)C.OOH → C2C=COOH + HO_2	9.82×10^{12} T^0 e^{-0T}	21.24
k_5	C2C(OOH)COO. → C2.C(OOH)COOH	3.66×10^{8} $T^{1.50}$ e^{-0T}	21.31
k_{-5}	C2.C(OOH)COOH → C2C(OOH)COO.	9.09×10^{9} $T^{0.22}$ $e^{-0.00109T}$	8.09
k_6	C2.C(OOH)COOH → CCyCOC(COOH) + OH	4.68×10^{11} T^0 e^{-0T}	20.00
k_7	C2.C(OOH)COOH → C=C(C)COOH + HO_2	3.05×10^{13} T^0 e^{-0T}	15.68
k_8	C2.C(OOH)COOH → C=C(OOH)C + CH_2OOH	2.84×10^{14} T^0 e^{-0T}	36.00
k_9	C2C(OOH)COO. → C2C(OO.)COOH	4.23×10^{12} $T^{-1.26}$ $e^{0.000160T}$	11.46
k_{-9}	C2C(OO.)COOH → C2C(OOH)COO.	3.54×10^{12} $T^{-1.24}$ e^{-0T}	14.57
k_{10}	C2C(OO.)COOH → C2C.COOH + O_2	2.08×10^{15} T^0 e^{-0T}	35.37
k_{11}	C2C(OO.)COOH → C=C(C)COOH + HO_2	1.73×10^{11} $T^{1.22}$ e^{-0T}	37.27
k_{12}	C2C(OO.)COOH → C2C=COOH + HO_2	5.75×10^{10} $T^{1.22}$ e^{-0T}	37.91

frequency/degeneracy (CPFIT)
C2C(OOH)COO.: 100.3 (12.287); 1038.0 (19.413); 2858.4 (10.300)
C2C(OOH)C.OOH: 100.1 (13.652); 1056.4 (19.084); 2833.5 (8.765)
C2.C(OOH)COOH: 100.4 (12.975); 1031.0 (19.408); 2821.6 (9.117)
C2C(OO.)COOH: 100.6 (12.290); 1031.9 (19.577); 2928.8 (10.133)
Lennard-Jones parameter
σ(Å) = 6.14, ε/k (K) = 678.63

k_1 taken from 88 XI

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -31.73 kcal mol^{-1}.

k_2 A_f estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}(T)/R$), deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (9.63) + ΔH_{rxn} (8.60) kcal mol^{-1}.

k_{-2} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 8.60 kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.5 \times 10^{11}$ = 1/2(C=C + HO_2), 72 KER/PAR. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 13.44 kcal mol^{-1} $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_5 A_f estimated using TST, A = (deg.) A' T^n, deg. = 6, A' = 6.106×10^7, n = 1.497, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (0) + E_{abst} (8.09) + ΔH_{rxn} (13.22) kcal mol^{-1}.

k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 13.22 kcal mol^{-1}.

k_6 A_f estimated using TST, A = (deg.) (ek_bT/h) exp($\Delta S^{\neq}(T)/R$), deg. = 1, ek_bT/h = $10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.5 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 7.88 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 28.2 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_9 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = -3.11 kcal mol^{-1}.

k_{-9} A_r estimated using TST, A = (deg.) A' T^n, deg. = 1, A' = 3.537×10^{12}, n = -1.244, A' and n are from thermal reaction analysis (AFACT2f) based on the

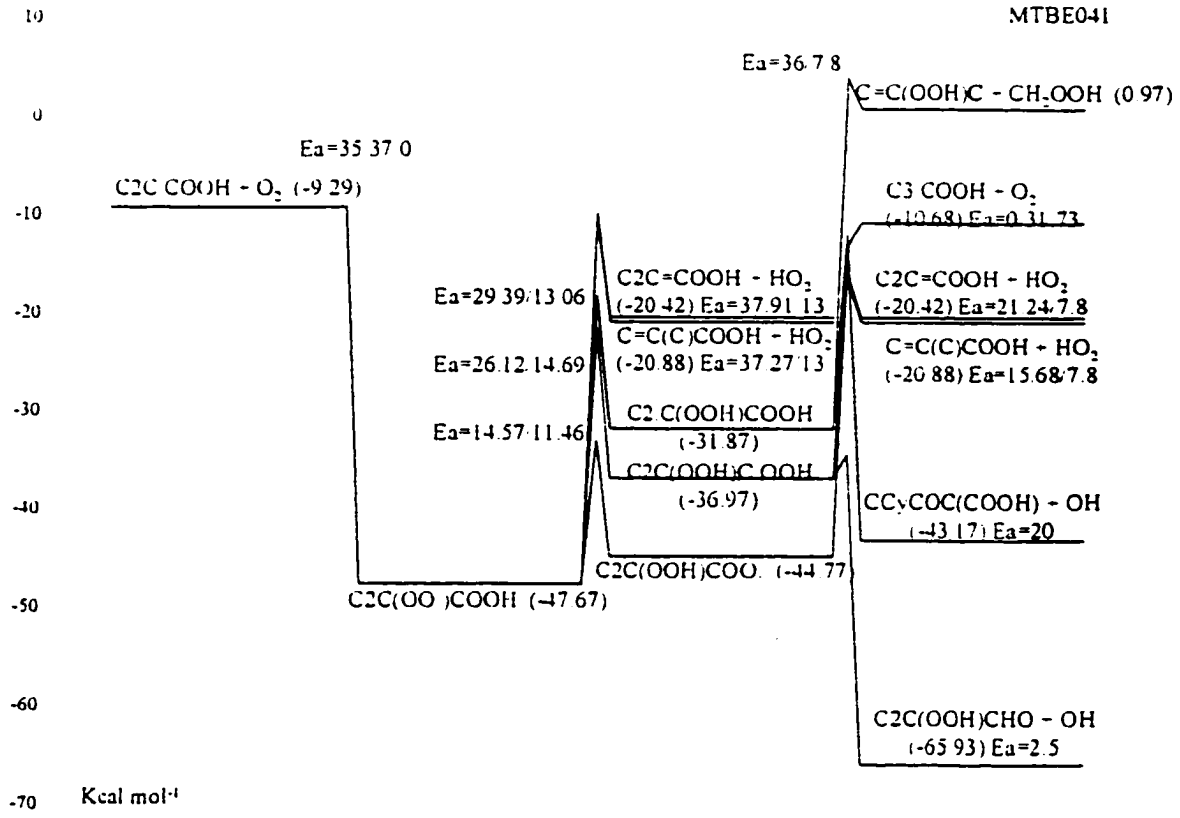
thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,r}$ = RS (6) + E_{abst} (11.46) -6 (H bond) - ΔU_{rxn} (-3.11) kcal mol^{-1}.

k_{10} A_f via A_r and Microscopic Reversbility (MR), A_r = 1.81 × 10^{12}, 92 WAL/AND for C3C. + O_2 → C3COO.. $E_{a,f}$ = ΔU_{rxn}, = 35.37 kcal mol^{-1}.

k_{11} A_f estimated using TST, A = (deg.) A' T^n, deg. = 6, A' = 2.876 × 10^{10}, n = 1.220, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r}$ + ΔU_{rxn}, $E_{a,r}$ is estimated as 13 kcal mol^{-1} in this study, ΔU_{rxn} = 24.27 kcal mol^{-1}.

k_{12} A_f estimated using TST, A = (deg.) A' T^n, deg. = 2, A' = 2.876 × 10^{10}, n = 1.220, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r}$ + ΔU_{rxn}, $E_{a,r}$ is estimated as 13 kcal mol^{-1} in this study, ΔU_{rxn} = 24.91 kcal mol^{-1}.

IID. 12 C2C.COOH + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C.COOH + O_2 → C2C(OO.)COOH	1.81×10^{12} T^0 e^{-0T}	0.00
k_{-1}	C2C(OO.)COOH → C2C.COOH + O_2	2.08×10^{15} T^0 e^{-0T}	35.37
k_2	C2C(OO.)COOH → C=C(C)COOH + HO_2	1.73×10^{11} $T^{1.22}$ e^{-0T}	37.27
k_3	C2C(OO.)COOH → C2C=COOH + HO_2	5.75×10^{10} $T^{1.22}$ e^{-0T}	37.91
k_4	C2C(OO.)COOH → C2C(OOH)C.OOH	2.78×10^{7} $T^{2.03}$ e^{-0T}	26.12
k_{-4}	C2C(OOH)C.OOH → C2C(OO.)COOH	4.04×10^{9} $T^{0.74}$ $e^{-0.00076T}$	14.69
k_5	C2C(OOH)C.OOH → C2C(OOH)CHO + OH	3.22×10^{13} T^0 e^{-0T}	2.50
k_6	C2C(OOH)C.OOH → C2C=COOH + HO_2	9.82×10^{12} T^0 e^{-0T}	21.24
k_7	C2C(OO.)COOH → C2.C(OOH)COOH	1.08×10^{9} $T^{1.83}$ e^{-0T}	29.39
k_{-7}	C2.C(OOH)COOH → C2C(OO.)COOH	3.21×10^{10} $T^{0.53}$ $e^{-0.00093T}$	13.06
k_8	C2.C(OOH)COOH → CCyCOC(COOH) + OH	4.68×10^{11} T^0 e^{-0T}	20.00
k_9	C2.C(OOH)COOH → C=C(C)COOH + HO_2	3.05×10^{13} T^0 e^{-0T}	15.68
k_{10}	C2.C(OOH)COOH → C=C(OOH)C + CH_2O	2.84×10^{14} T^0 e^{-0T}	36.00
k_{11}	C2C(OO.)COOH → C2C(OOH)COO.	3.54×10^{12} $T^{-1.24}$ e^{-0T}	14.57
k_{-11}	C2C(OOH)COO. → C2C(OO.)COOH	4.23×10^{12} $T^{-1.26}$ $e^{0.00016T}$	11.46

	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_{12}	C2C(OOH)COO. → C3 COOH + O_2	2.31×10^{14} T^0 e^{-0T}	31.73

frequency/degeneracy (CPFIT)
C2C(OO.)COOH: 100.6 (12.290); 1031.9 (19.577); 2928.8 (10.133)
C2C(OOH)C.OOH: 100.1 (13.652); 1056.4 (19.084); 2833.5 (8.765)
C2 C(OOH)COOH: 100.4 (12.975); 1031.0 (19.408); 2821.6 (9.117)
C2C(OOH)COO.: 100.3 (12.287); 1038.0 (19.413); 2858.4 (10.300)
Lennard-Jones parameter
σ(Å) = 6.14, ε/k (K) = 678.63

k_1 92 WAL/AND for C3C. + O_2 → C3COO.).

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -35.37 kcal mol^{-1}.

k_2 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 6, A′ = 2.876×10^{10}, n = 1.220, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r} + \Delta U_{rxn}$, $E_{a,r}$ is estimated as 13 kcal mol^{-1} in this study, ΔU_{rxn} = 24.27 kcal mol^{-1}.

k_3 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 2, A′ = 2.876×10^{10}, n = 1.220, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r} + \Delta U_{rxn}$, $E_{a,r}$ is estimated as 13 kcal mol^{-1} in this study, ΔU_{rxn} = 24.91 kcal mol^{-1}.

k_4 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 2, A′ = 1.390×10^{7}, n = 2.032, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (6) + E_{abst} (8.69) + ΔH_{rxn} (11.43) kcal mol^{-1}.

k_{-4} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 11.43 kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.5 \times 10^{11}$ = 1/2(C=C + HO_2), 72 KER/PAR. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 13.44 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_7 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 6, A′ = 1.802×10^{8}, n = 1.832, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (6) + E_{abst} (7.06) + ΔH_{rxn} (16.33) kcal mol^{-1}.

k_{-7} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 16.33 kcal mol^{-1}.

k_8 A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4 3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_9 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.5 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 7.88 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1} (estimated by Bozzelli).

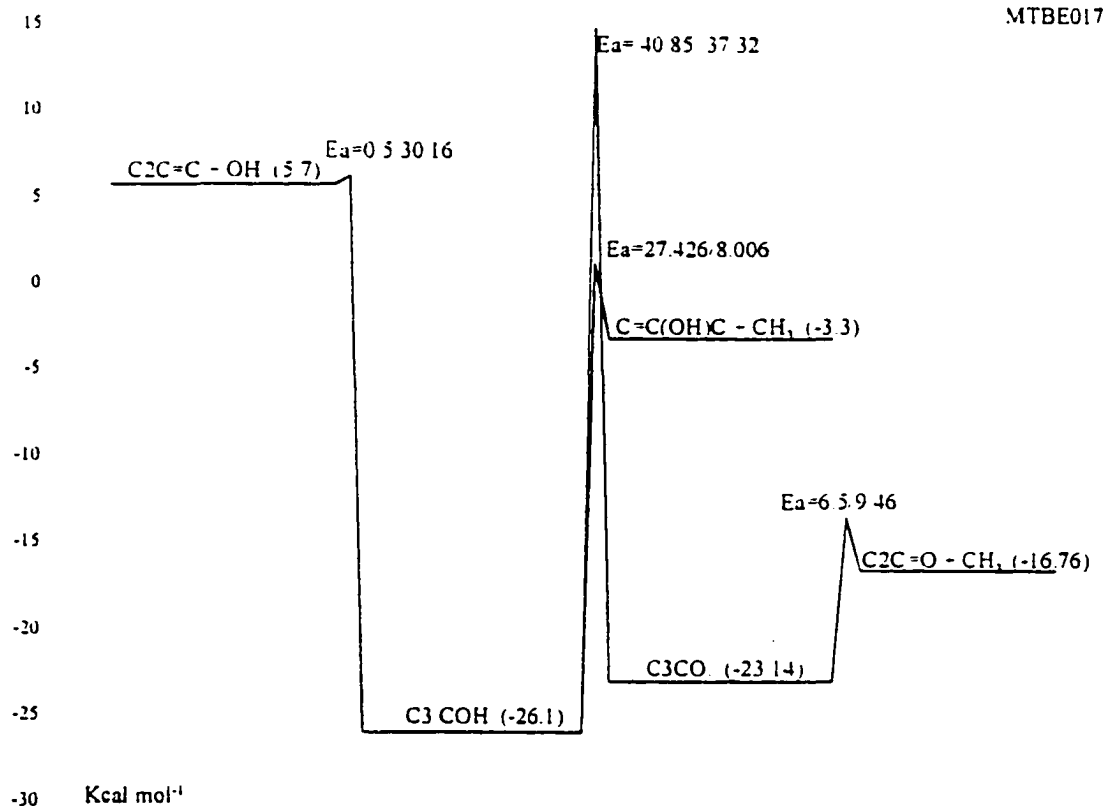
k_{10} A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 28.2 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_{11} A_f estimated using TST, A = (deg.) $A' T^n$, deg. = 1, $A' = 3.537 \times 10^{12}$, n = -1.244, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (6) + E_{abst} (11.46) - 6 (H bond) + ΔU_{rxn} (3.11) kcal mol^{-1}.

k_{-11} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 3.11 kcal mol^{-1}.

k_{12} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.0 \times 10^{12}$, 88 XI for C3CC. + $O_2 \rightarrow$ C3CCOO.. $E_{a,f} = \Delta U_{rxn}$, = 31.73 kcal mol^{-1}.

IID. 13 C2C=C + OH → [C3.COH]* → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C=C + OH → C3.COH	2.92×10^{12} T^0 e^{-0T}	0.50
k_{-1}	C3.COH → C2C=C + OH	2.12×10^{13} T^0 e^{-0T}	30.16
k_2	C3.COH → C=C(OH)C + CH_3	6.72×10^{12} $T^{1.0}$ e^{-0T}	27.43
k_3	C3.COH → C3CO.	5.92×10^{7} $T^{1.01}$ $e^{-0.00049T}$	40.85
k_{-3}	C3CO. → C3.COH	6.72×10^{9} $T^{1.0}$ e^{-0T}	37.32
k_4	C3CO. → C2C=O + CH_3	3.20×10^{14} T^0 e^{-0T}	9.46

frequency/degeneracy (CPFIT)
C3.COH: 442.8 (11.944); 1273.0 (12.834); 2967.6 (9.222)
C3CO.: 452.6 (11.685); 1274.7 (14.286); 2979.3 (8.528)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f estimated as 1/2 (C_3H_6 + OH), 91 TSA. $E_{a,f}$ estimated as 0.5 kcal mol^{-1} by

Bozzelli

k_1 A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, $\Delta U_{rxn} = -29.66$ kcal mol^{-1}.

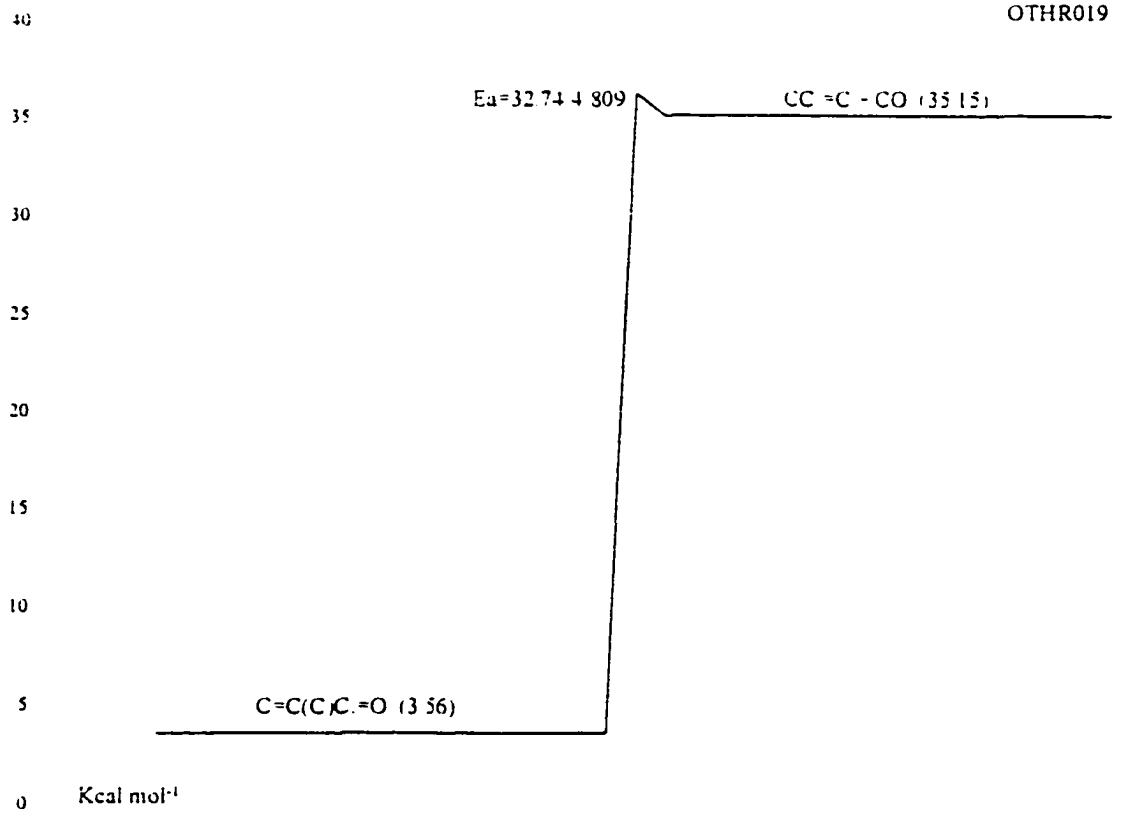
k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for $C_3H_6 + CH_3 \rightarrow C3.C$. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 19.42$ kcal mol^{-1}. $E_{a,r} = 8.006$ kcal mol^{-1}. (referenced as the same as the A_r).

k_3 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 3.53$ kcal mol^{-1}.

k_{-3} A_r estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 9, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotors (-4.3 cal mol^{-1} K^{-1}). $E_{a,f} = RS\ (26) + E_{abst}\ (11.32)$ kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.16 \times 10^{11}$ Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 2.96$ kcal mol^{-1}. $E_{a,r} = 6.5$ kcal mol^{-1}. (estimated by Bozzelli).

IID. 14 C2C=C + OH → [C2C.COH]* → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C=C + OH → C2C.COH	2.92×10^{12} T^0 e^{-0T}	0.00
k_{-1}	C2C.COH → C2C=C + OH	1.95×10^{13} T^0 e^{-0T}	28.52
k_2	C2C.COH → C2C=COH + H	1.64×10^{12} $T^{1.0}$ e^{-0T}	33.43
k_3	C2C.COH → C=C(C)COH + H	8.30×10^{13} T^0 e^{-0T}	38.15

frequency/degeneracy (CPFIT)
C2C.COH: 389.3 (10.799); 1475.6 (15.383); 3185.2 (7.818)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f estimated as 1/2 (C_3H_6 + OH), 91 TSA. $E_{a,f}$ estimated as 0 kcal mol^{-1} by Bozzelli

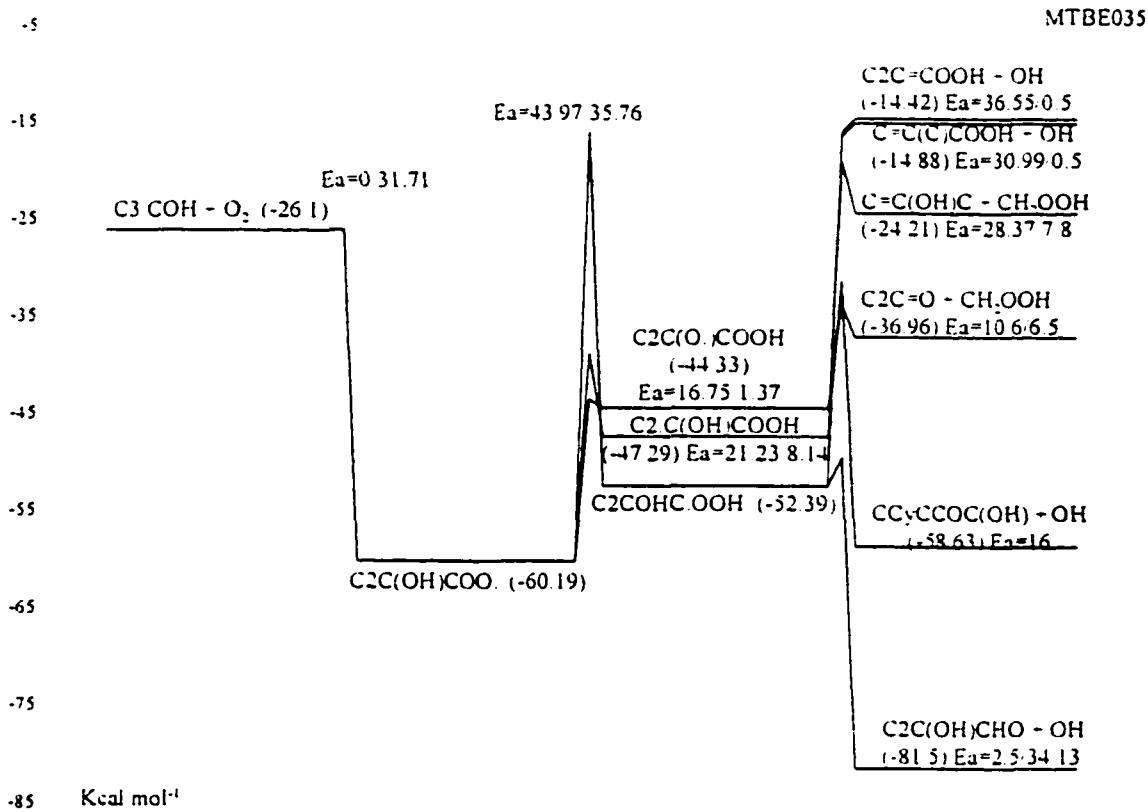
k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -28.52 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.615 \times 10^{12}$ = 1/2 (C_3H_6 + H

→ CCC.), 91 TSA. $E_{3,f} = E_{3,r} - \Delta U_{rxn}$, $\Delta U_{rxn} = 30.52$ kcal mol^{-1} $E_{3,r} = 2.906$ kcal mol^{-1}. (referenced as the same as the A_r).

k_3 90 TSA for C3C. → C2C=C + H

IID. 15 C3.COH + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C3.COH + O_2 → C2C(OH)COO.	1.00×10^{12} T^0 e^{-0T}	0.00
k_{-1}	C2C(OH)COO. → C3.COH + O_2	2.30×10^{14} T^0 e^{-0T}	31.71
k_2	C2C(OH)COO. → C2C(OH)C.OOH	6.13×10^{9} $T^{1.17}$ e^{-0T}	43.97
k_{-2}	C2C(OH)C.OOH → C2C(OH)COO.	5.32×10^{11} $T^{-0.30}$ $e^{-0.00121T}$	35.76
k_3	C2C(OH)C.OOH → C2C(OH)CHO + OH	7.53×10^{12} T^0 e^{-0T}	2.50
k_4	C2C(OH)C.OOH → C2C=COOH + OH	1.42×10^{13} T^0 e^{-0T}	36.55
k_5	C2C(OH)COO. → C2.C(OH)COOH	7.58×10^{8} $T^{1.08}$ e^{-0T}	21.23
k_{-5}	C2.C(OH)COOH → C2C(OH)COO.	2.68×10^{10} $T^{0.01}$ $e^{-0.00097T}$	8.14
k_6	C2.C(OH)COOH → C=C(OH)C + OH	4.38×10^{13} T^0 e^{-0T}	28.37
k_7	C2.C(OH)COOH → C=C(C)COOH + OH	6.31×10^{13} T^0 e^{-0T}	30.99
k_8	C2.C(OH)COOH → CCyCCOC (OH) + OH	4.25×10^{10} $T^{0.18}$ e^{-0T}	16.00
k_9	C2C(OH)COO. → C2C(O.)COOH	7.56×10^{7} $T^{1.06}$ e^{-0T}	16.75
k_{-9}	C2C(O.)COOH → C2C(OH)COO.	2.14×10^{9} $T^{0.36}$ $e^{-0.00113T}$	1.37
k_{10}	C2C(O.)COOH → C2C=O + CH_2OOH	6.96×10^{14} T^0 e^{-0T}	10.60

frequency/degeneracy (CPFIT)
C2C(OH)COO.. 270.0 (12.085); 1109.5 (16.601), 2859.8 (10.814)
C2.C(OH)COOH. 298.6 (13.666); 1139.6 (15.948); 2851.4 (9.386)
C2C(OH)C.OOH: 278.7 (13.932); 1159.7 (16.043); 2864.7 (9.025)
C2C(O.)COOH: 277.7 (12.704); 1121.3 (17.851), 2824.5 (8.945)
Lennard-Jones parameter
σ(Å) = 5.86, ε/k (K) = 632.06

k_1 taken from 88 XI for C3CC. + $O_2 \rightarrow$ C3CCOO.).

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -31.71 kcal mol^{-1}.

k_2 A_f estimated using TST, A = (deg.) A' T^n, deg. = 2, A' = 3.116×10^9, n = 1.174, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (26) + E_{abst} (9.76) + ΔH_{rxn} (8.21) kcal mol^{-1}.

k_{-2} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 8.21 kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O$ + OH (1990 Page)

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.46 \times 10^{12}$ = 1/4(C=C + OH),. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 36.05 kcal mol^{-1}. $E_{a,r}$ = 0.5 kcal mol^{-1}. (estimated by Bozzelli).

k_5 A_f estimated using TST, A = (deg.) A' T^n, deg. = 6, A' = 1.263×10^8, n = 1.084, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (0) + E_{abst} (8.14) + ΔH_{rxn} (13.09) kcal mol^{-1}.

k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 13.09 kcal mol^{-1}.

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 20.57 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.92 \times 10^{12}$, 91 TSA for C_3H_6 + OH $\rightarrow$ Prod.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 30.49 kcal mol^{-1}. $E_{a,r}$ = 0.5 kcal mol^{-1}. (estimated by Bozzelli).

k_8 A_f estimated using TST, A = (deg.) A' T^n, deg. = 1, A' = 4.253×10^{10}, n = 0.183, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ is estimated in this study.

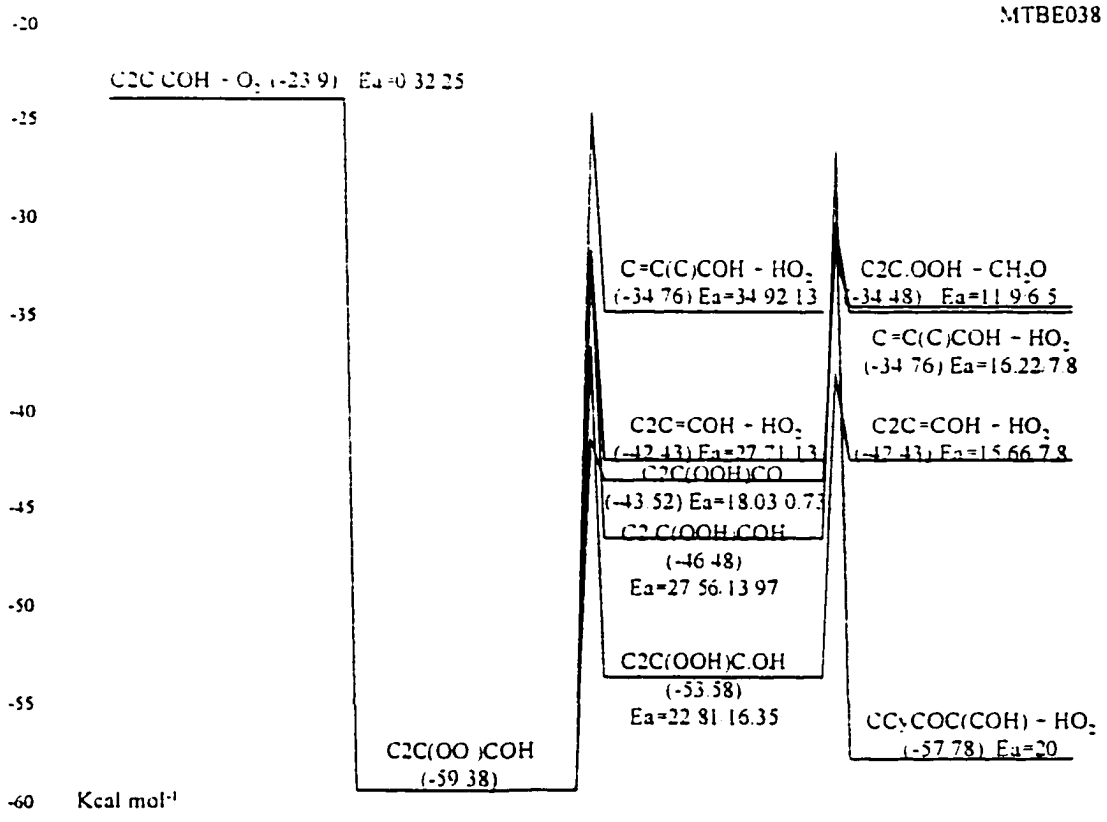
k_9 A_f estimated using TST, A = (deg.) A' T^n, deg. = 1, A' = 7.559×10^7, n = 1.062, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal

rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (0) − E_{abst} (7.37) - 6 (H bond) − ΔH_{rxn} (15.38) kcal mol^{-1}.

k_9 A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 15.38 kcal mol^{-1}.

k_{10} A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.16 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} - \Delta U_{rxn}$, ΔU_{rxn} = 4.10 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (estimated by Bozzelli).

IID. 16 C2C.COH + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C.COH + O_2 → C2C(OO.)COH	1.81×10^{12} T^0 e^{-0T}	0.00
k_{-1}	C2C(OO.)COH → C2C.COH + O_2	1.02×10^{15} T^0 e^{-0T}	32.25
k_2	C2C(OO.)COH → C=C(C)COH + HO_2	1.73×10^{11} $T^{1.22}$ e^{-0T}	34.92
k_3	C2C(OO.)COH → C2C=COH + HO_2	5.75×10^{10} $T^{1.22}$ e^{-0T}	27.71
k_4	C2C(OO.)COH → C2C(OOH)C.OH	4.66×10^{8} $T^{1.36}$ e^{-0T}	22.81
k_{-4}	C2C(OOH)C.OH → C2C(OO.)COH	1.44×10^{11} $T^{-0.05}$ $e^{-0.00093T}$	16.35
k_5	C2C(OOH)C.OH → C2C=COH + HO_2	3.18×10^{11} T^0 e^{-0T}	15.66
k_6	C2C(OO.)COH → C2.C(OOH)COH	2.30×10^{10} $T^{1.07}$ e^{-0T}	27.56
k_{-6}	C2.C(OOH)COH → C2C(OO.)COH	1.03×10^{12} $T^{-0.33}$ $e^{-0.0009T}$	13.97
k_7	C2.C(OOH)COH → C=C(C)COH + HO_2	2.09×10^{13} T^0 e^{-0T}	16.22
k_8	C2.C(OOH)COH → CCyCOC(COH) + OH	4.68×10^{11} T^0 e^{-0T}	20.00
k_9	C2C(OO.)COH → C2C(OOH)CO.	4.22×10^{7} $T^{1.18}$ e^{-0T}	18.03
k_{-9}	C2C(OOH)CO. → C2C(OO.)COH	1.70×10^{11} $T^{-0.18}$ $e^{-0.00019T}$	0.73
k_{10}	C2C(OOH)CO. → C2C.OOH + CH_2O	8.22×10^{13} T^0 e^{-0T}	11.90

frequency/degeneracy (CPFIT)
C2C(OO.)COH: 291.4 (12.538); 1135.9 (16.437); 2997.8 (10.525)
C2.C(OOH)COH: 312.6 (14.003); 1162.7 (15.884); 3008.3 (9.113)
C2C(OOH)C.OH: 309.2 (14.390); 1147.0 (15.883); 3022.3 (8.727)
C2C(OOH)CO.: 295.9 (13.107); 1144.8 (17.750); 2992.0 (8.643)
Lennard-Jones parameter
σ(Å) = 5.86, ε/k (K) = 632.06

k_1 92 WAL/AND for C3C. + O_2 → C3COO.).

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -32.25 kcal mol^{-1}.

k_2 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 6, A′ = 2.876 × 10^{10}, n = 1.22, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r} + \Delta U_{rxn}$, $E_{a,r}$ is estimated as 13 kcal mol^{-1} in this study, ΔU_{rxn} = 21.92 kcal mol^{-1}.

k_3 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 2, A′ = 2.876 × 10^{10}, n = 1.22, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ via $E_{a,r} + \Delta U_{rxn}$, $E_{a,r}$ is estimated as 13 kcal mol^{-1} in this study, ΔU_{rxn} = 14.71 kcal mol^{-1}.

k_4 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 2, A′ = 2.328 × 10^8, n = 1.358, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (6) + E_{abst} (10.35) + ΔH_{rxn} (6.46) kcal mol^{-1}.

k_{-4} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 6.46 kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.5 \times 10^{11} = 1/2(C{=}C + HO_2)$, 72 KER/PAR. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 7.86 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_6 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 6, A′ = 3.836 × 10^9, n = 1.071, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (6) + E_{abst} (7.97) + ΔH_{rxn} (13.59) kcal mol^{-1}.

k_{-6} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 13.59 kcal mol^{-1}.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.5 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 8.42 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

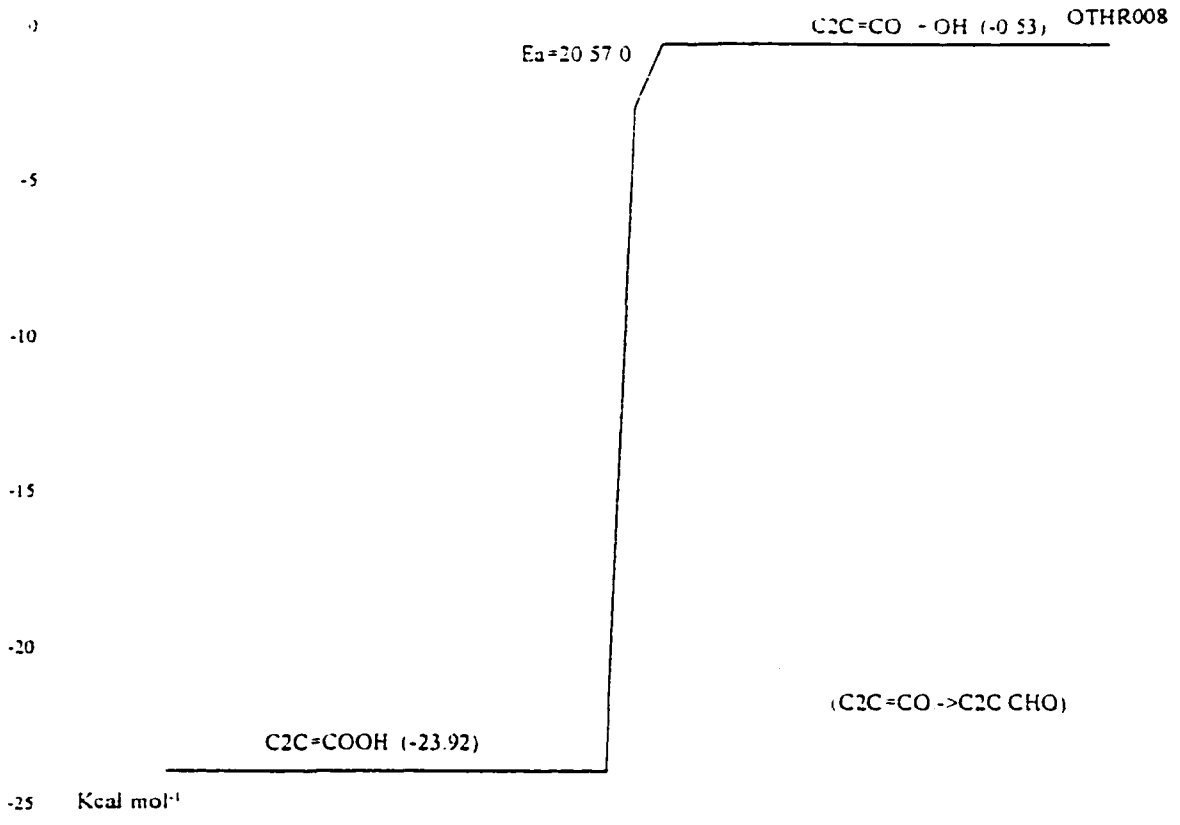
k_8 A_f estimated using TST, A = (deg.) $(ek_bT/h)\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_9 A_f estimated using TST, A = (deg.) A' T^n, deg. = 1, A' = 4.217 × 10^7, n = 1.184, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (0) + E_{abst} (6.73) - 6 (H bond) + ΔH_{rxn} (17.30) kcal mol^{-1}.

k_{-9} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 17.30 kcal mol^{-1}

k_{10} A_f via A_r and Microscopic Reversbility (MR), A_r = 2.41 × 10^{10} = 1/2 (CH_2OH + C=C → C CCOH), 87 TSA. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 5.40 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (estimated by Bozzelli).

IID. 17 C2C=COOH → C2C.CHO (C2C=CO.) + OH

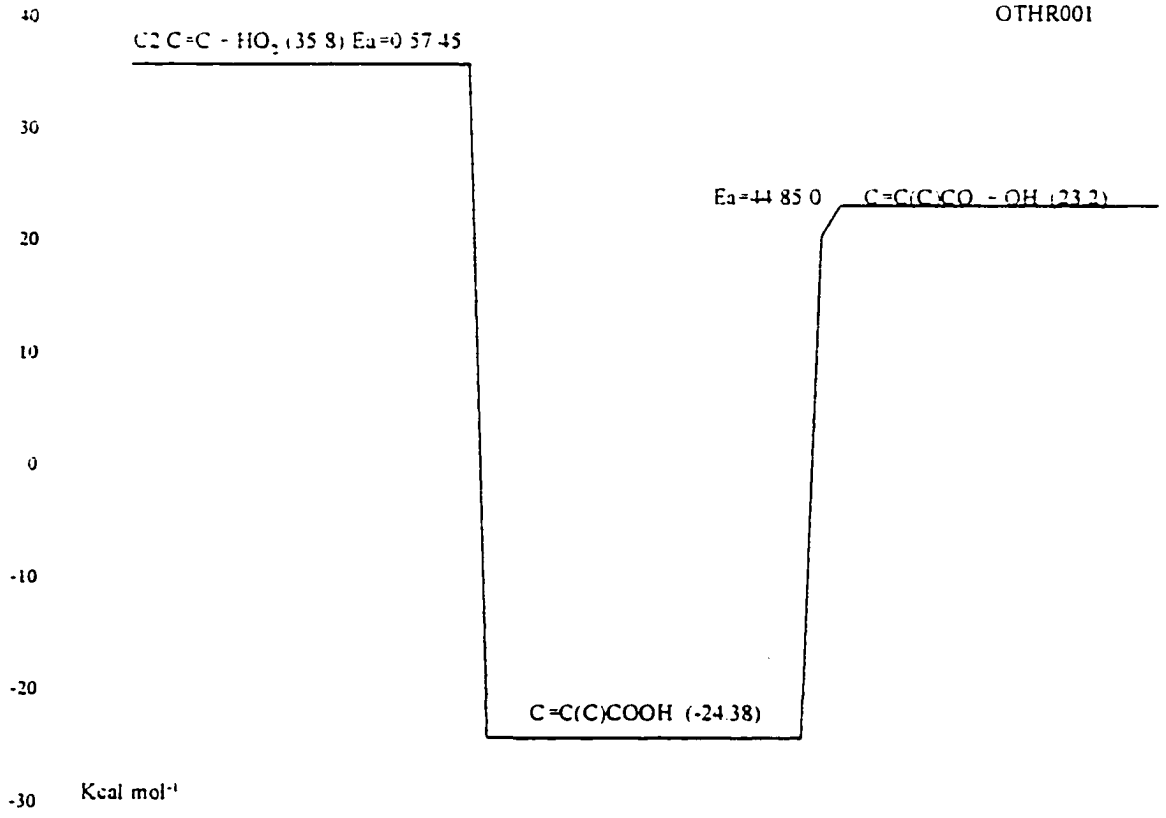


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C=COOH → C2C=CO. + OH	1.56×10^{15} T^0 e^{-0T}	20.57

frequency/degeneracy (CPFIT)
C2C=COOH: 337.9 (11.813); 1223.0 (14.753); 2824.6 (7.434)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 A_f via A_r and Microscopic Reversbility (MR), A_r = 1.51 × 10^{13}, 91 TSA for C=CC. + OH. $E_{a,f} = \Delta U_{rxn}$ = 20.57 kcal mol^{-1}.

IID. 18 C2.C=C + HO_2 → C=C(C)COOH → C=C(C)CO. + OH



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2.C=C + HO_2 → C=C(C)COOH	1.00×10^{13} T^0 e^{-0T}	0.00
k_{-1}	C=C(C)COOH → C2.C=C + HO_2	1.67×10^{15} T^0 e^{-0T}	57.45
k_2	C=C(C)COOH → C=C(C)CO. + OH	1.66×10^{15} T^0 e^{-0T}	44.85

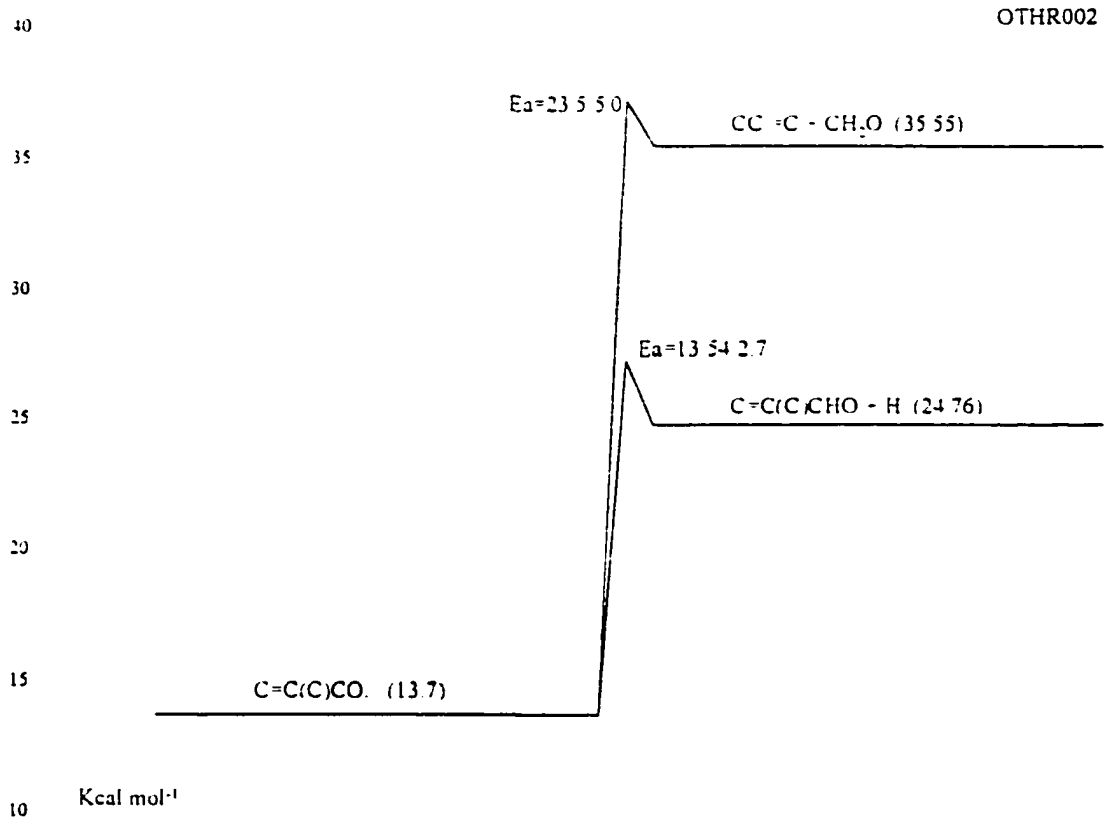
frequency/degeneracy (CPFIT)
C=C(C)COOH: 250.9 (10.249); 1109.7 (14.976); 2777.4 (8.775)
Lennard-Jones parameter
σ(Å) = 5.54, ε/k (K) = 584.86

k_1 A_f estimated as 1/2 (CH_3 + HO_2 → CH_3O + OH).

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -57.45 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, taken as the same as A for CH_3O + OH. $E_{a,f} = \Delta U_{rxn}$ = 44.85 kcal mol^{-1}.

IID. 19 C=C(C)CO. → Products



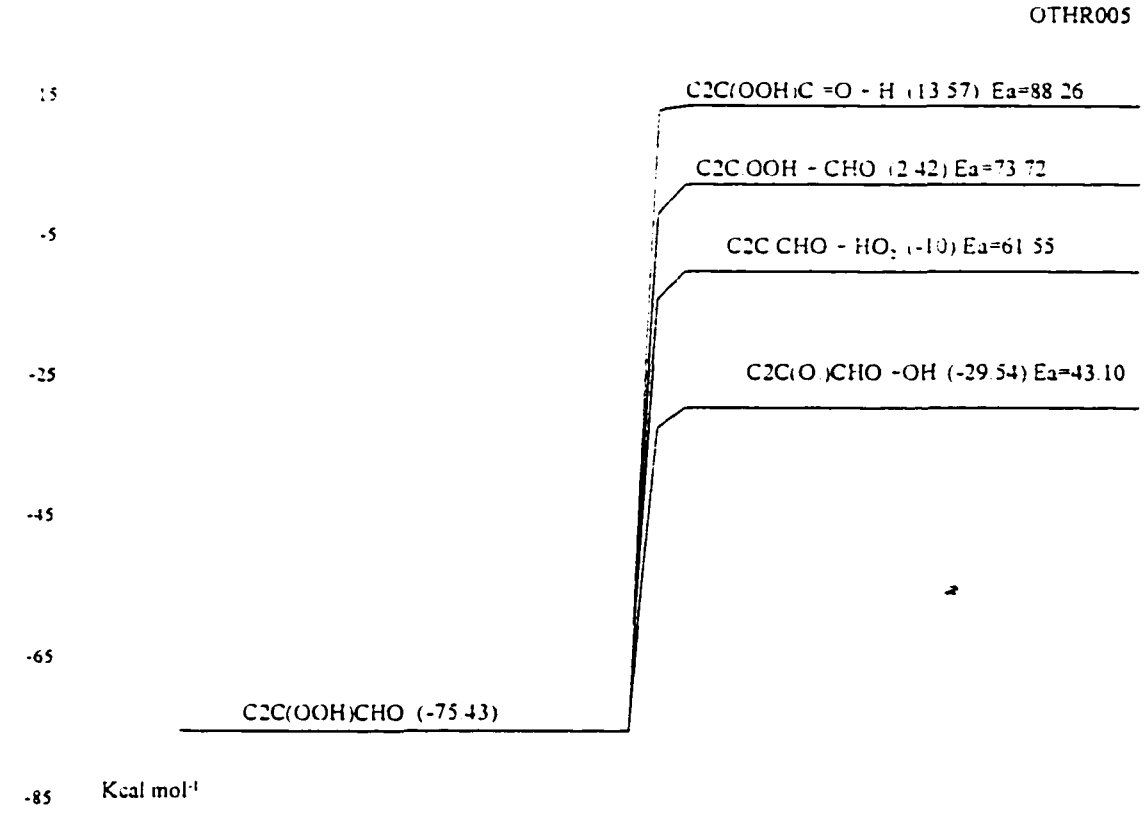
	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C=C(C)CO. → CC.=C + CH_2O	1.54×10^{13} T^0 e^{-0T}	23.50
k_2	C=C(C)CO. → C=C(C)CHO + H	4.18×10^{12} T^0 e^{-0T}	13.54

frequency/degeneracy (CPFIT)
C=C(C)CO.: 468.5 (11.349); 1549.9 (12.883); 3526.8 (4.768)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, taken as the same as A for CC.C + CH_2O → CCC + CHO. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 18.5 kcal mol^{-1}. $E_{a,r}$ = 5.0 kcal mol^{-1}. (estimated in this study).

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{12}$ = 1/2 (H + C=C). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 10.84 kcal mol^{-1}. $E_{a,r}$ = 2.7 kcal mol^{-1}. (estimated based on 84 WAR for H + CC=C → CCC.).

IID. 20 C2C(OOH)CHO → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C(OOH)CHO → C2C.OOH + CHO	3.35×10^{17} T^0 e^{-0T}	73.72
k_2	C2C(OOH)CHO → C2C.CHO + HO_2	3.45×10^{15} T^0 e^{-0T}	61.55
k_3	C2C(OOH)CHO → C2C(OOH)C.=O + H	1.02×10^{15} T^0 e^{-0T}	88.26
k_4	C2C(OOH)CHO → C2C(O.)CHO + OH	1.06×10^{15} T^0 e^{-0T}	43.10

frequency/degeneracy (CPFIT)
C2C(OOH)CHO: 251.1 (10.745); 1069.7 (17.622); 2476.7 (8.133)
Lennard-Jones parameter
σ(Å) = 5.86, ε/k (K) = 632.06

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, 88 TSA for CC.C + CHO → C2CCHO. $E_{a,f} = \Delta U_{rxn} = 73.72$ kcal mol^{-1}.

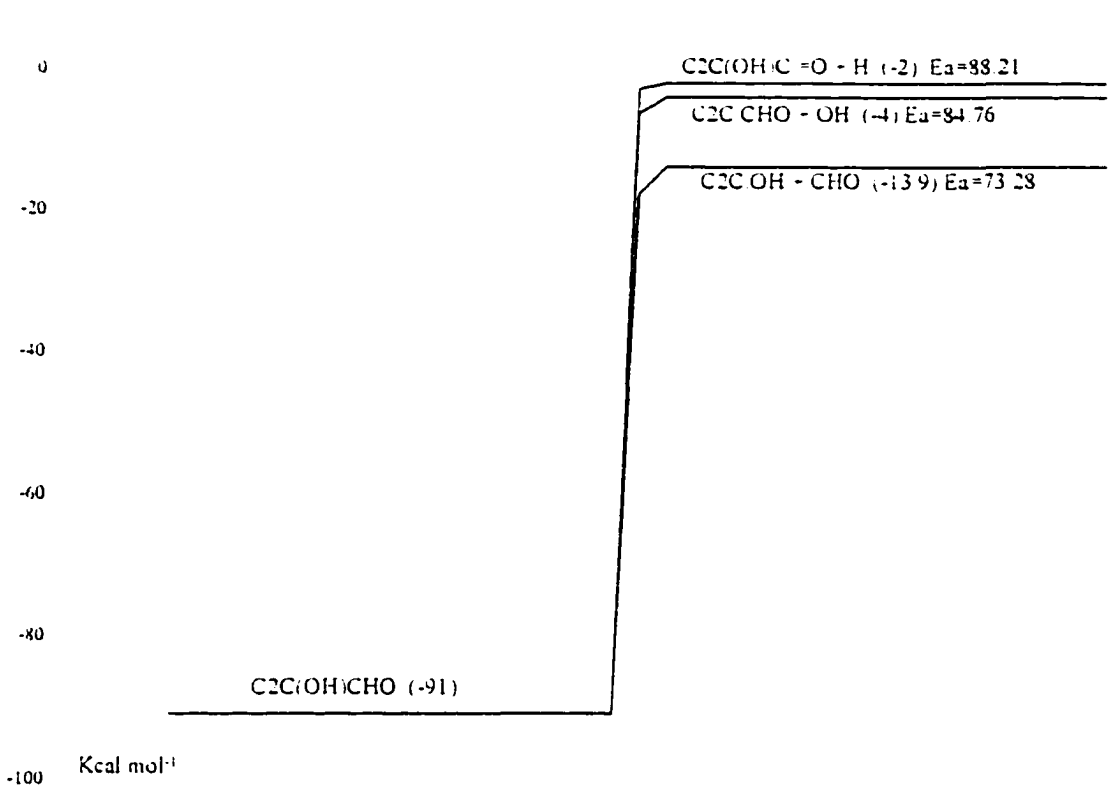
k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{13}$ = 1/2 (HO_2 + CH_3). $E_{a,f} = \Delta U_{rxn} = 61.55$ kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{13}$ 1/2 (H + CHO),

NIST FIT $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (88.26) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for $CH_3O + O$, $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (43.10) kcal mol^{-1}

IID. 21 C2C(OH)CHO → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C(OH)CHO → C2C.OH + CHO	4.48×10^{17} T^0 e^{-0T}	73.28
k_2	C2C(OH)CHO → C2C.CHO + OH	2.75×10^{15} T^0 e^{-0T}	84.76
k_2	C2C(OH)CHO → C2C(OH)C.=O + H	9.83×10^{14} T^0 e^{-0T}	88.21

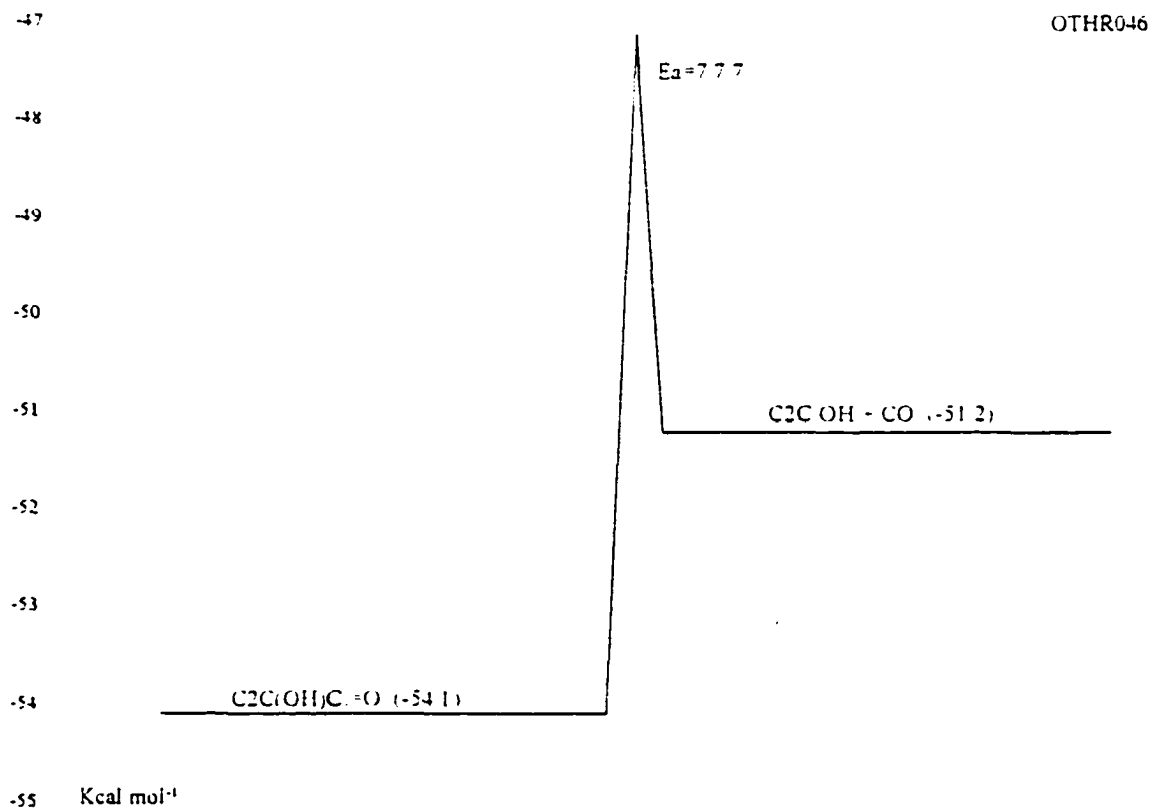
frequency/degeneracy (CPFIT)
C2C(OH)CHO: 417.6 (12.380); 1378.6 (16.307); 3379.2 (5.313)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, 88 TSA for CC.C + CHO → C2CCHO. $E_{a,f} = \Delta U_{rxn} = 73.28$ kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 7.55 \times 10^{12}$ = 1/2 (OH + C=CC.), 86 TSA. $E_{a,f} = \Delta U_{rxn} = 84.76$ kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{13}$ 1/2 (H + CHO), NIST FIT. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (88.21) kcal mol^{-1}.

IID. 22 C2C(OH)C.=O → C2C.OH + CO

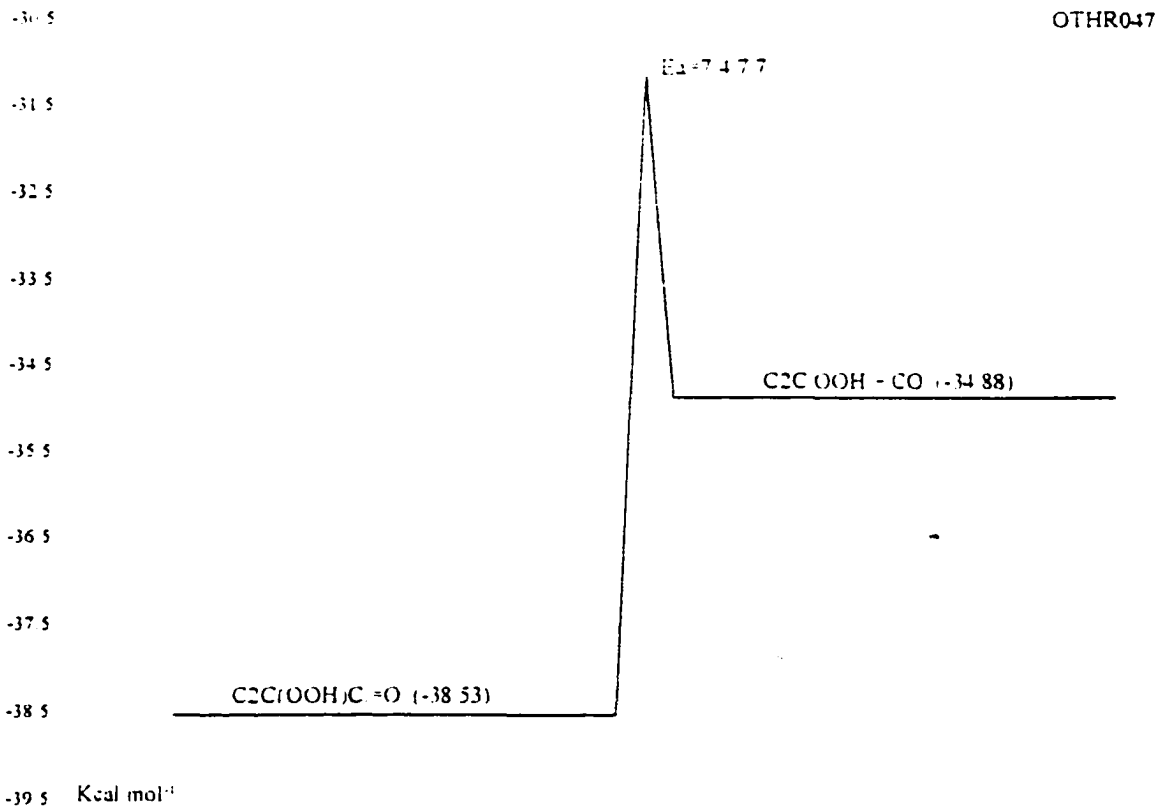


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C(OH)C.=O → C2C.OH + CO	7.22×10^{13} T^{0} e^{-0T}	7.00

frequency/degeneracy (CPFIT)
C2C(OH)C.=O: 412.6 (11.980); 1408.4 (14.872); 3549.7 (4.148)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{11}$, 72 KER/PAR for C3C. + C_2H_2. $E_{a,f} = E_{a,f}$ (7.7) + ΔU_{rxn} (-0.68) kcal mol^{-1}.

IID. 23 C2C(OOH)C.=O → C2C.OOH + CO

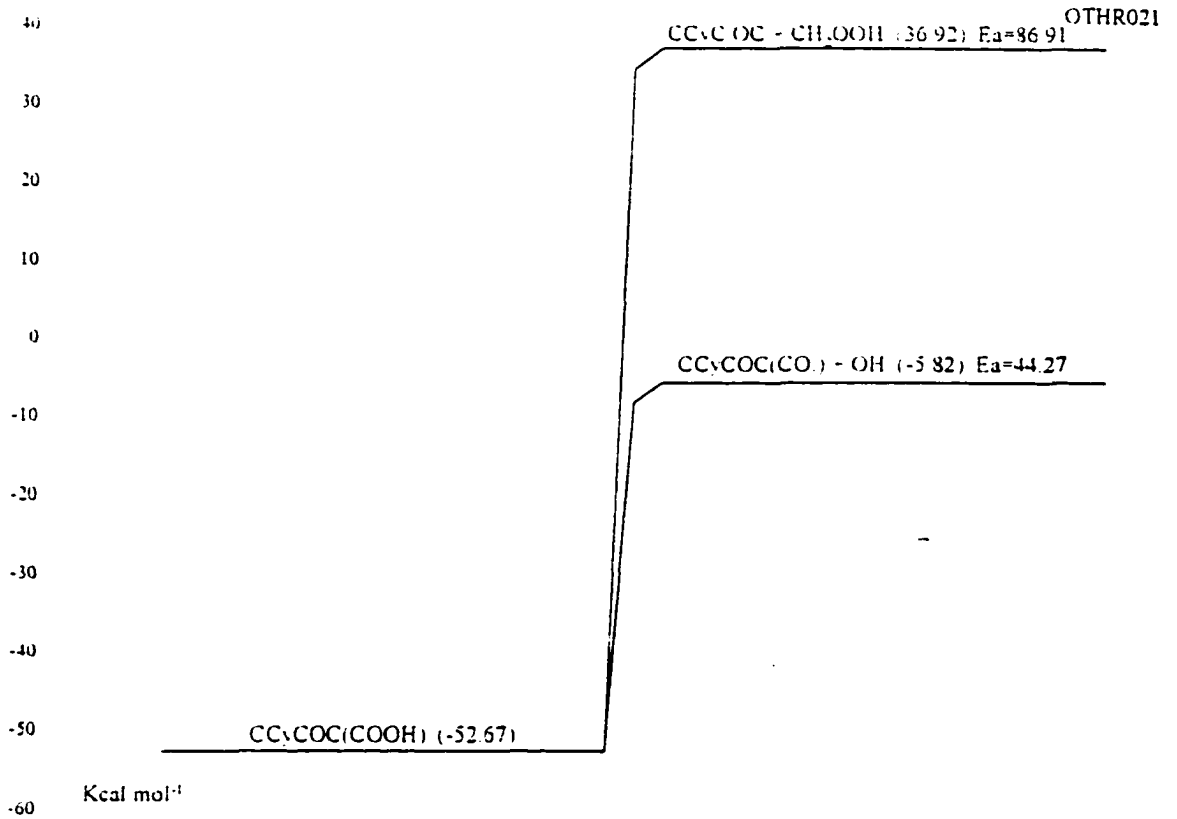


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C(OOH)C.=O → C2C.OOH + CO	5.23×10^{13} T^0 e^{-0T}	7.40

frequency/degeneracy (CPFIT)
C2C(OOH)C.=O: 250.0 (10.700); 1079.7 (15.893); 2400.1 (6.907)
Lennard-Jones parameter
σ(Å) = 5.86, ε/k (K) = 632.06

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{11}$, 72 KER/PAR for C3C. + C_2H_2. $E_{a,f} = E_{a,r}$ (7.7) + ΔU_{rxn} (-0.29) kcal mol^{-1}.

IID. 24 CCyCOC(COOH) → Products



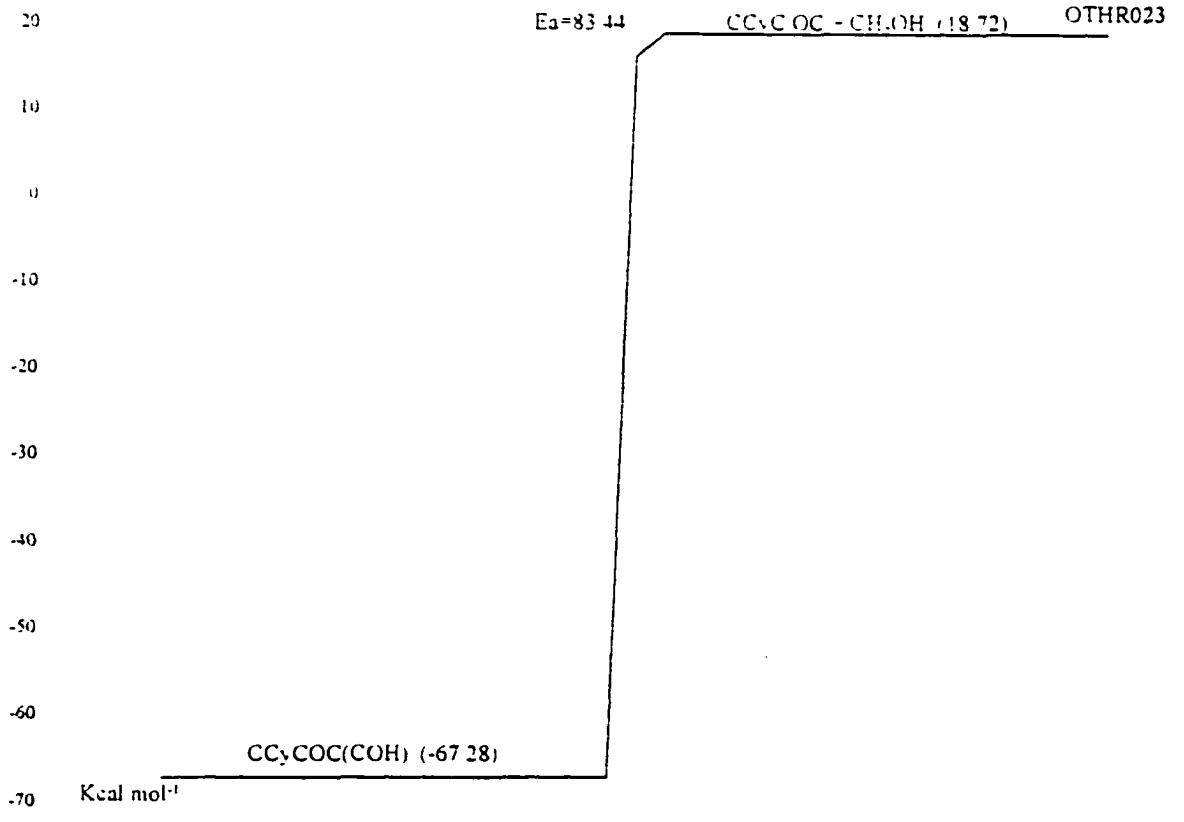
	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CCyCOC(COOH) → CCyC.OC + CH_2OOH	8.02×10^{16} T^0 e^{-0T}	86.91
k_2	CCyCOC(COOH) → CC̄yCOC(CO.) + OH	1.98×10^{15} T^0 e^{-0T}	44.27

frequency/degeneracy (CPFIT)
CCyCOC(COOH): 250.9 (9.960); 1066.2 (19.075); 2811.3 (7.964)
Lennard-Jones parameter
σ(Å) = 5.86, ε/k (K) = 632.06

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{12} = 1/3$ (C3C. + CH_2OH), 91 TSA. $E_{a,f} = \Delta U_{rxn} = 86.91$ kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 91 TSA for OH + C=CC.. $E_{a,f} = \Delta U_{rxn} = 44.27$ kcal mol^{-1}.

IID. 25 CCyCOC(COH) → Products

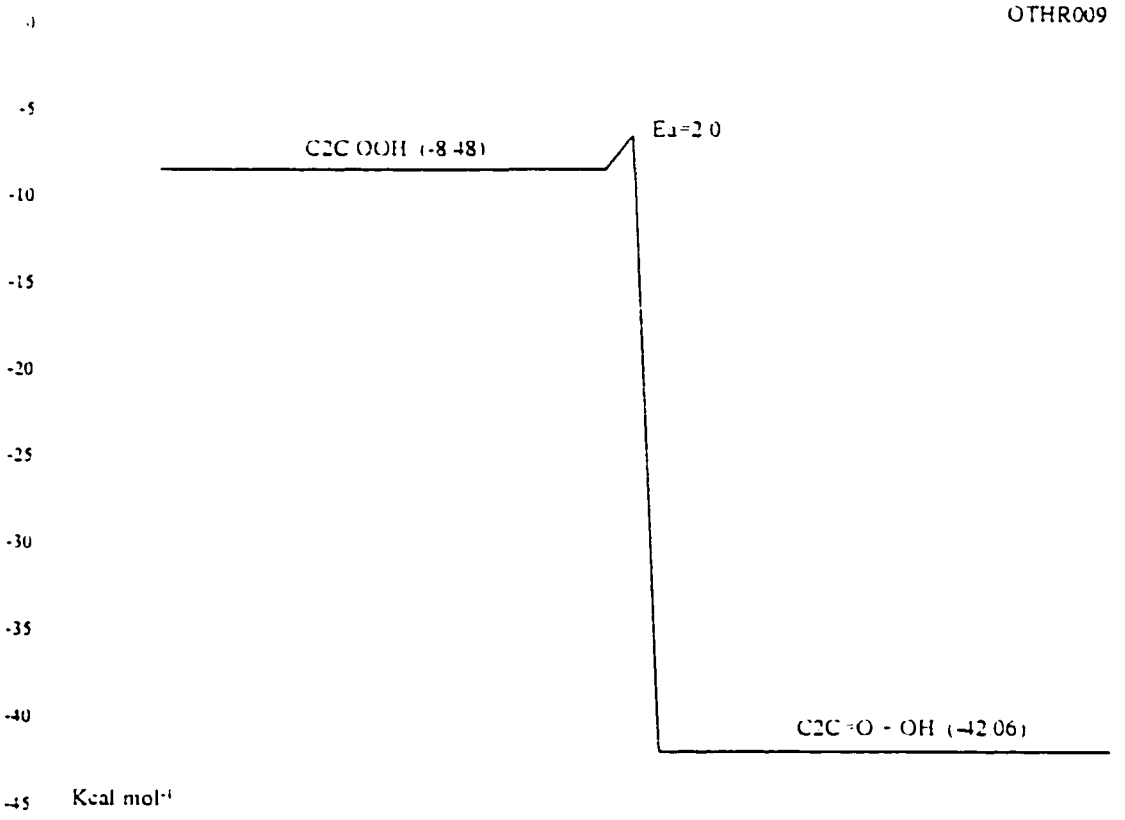


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CCyCOC(COH) → CCyC OC + CH_2OH	5.98×10^{16} T^0 e^{-0T}	83.44

frequency/degeneracy (CPFIT)
CCyCOC(COH): 479.0 (12.212); 1268.8 (14.955); 3148.6 (7.334)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{12} = 1/2$ (C3C. + CH_2OH), 91 TSA. $E_{a,f} = \Delta U_{rxn} = 83.44$ kcal mol^{-1}.

IID. 26 C2C.OOH → C2C=O + OH

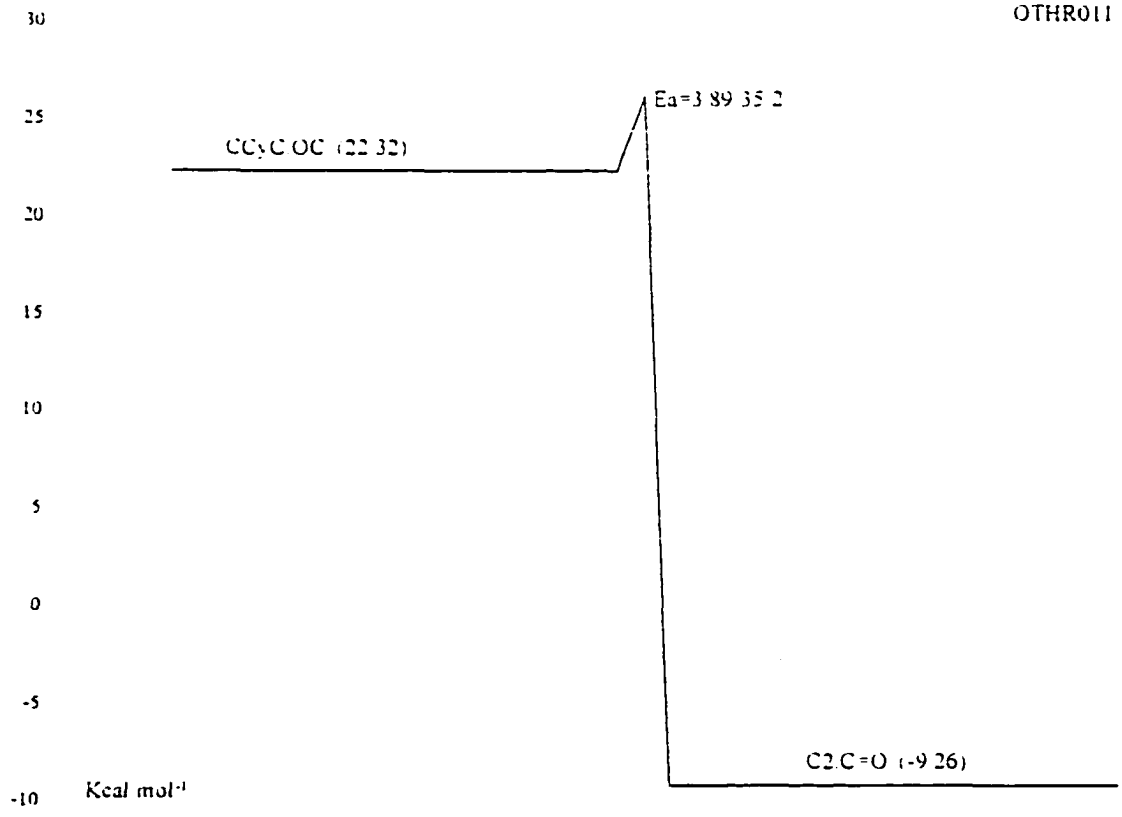


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C.OOH → C2C=O + OH	4.48×10^{12} T^0 e^{-0T}	2.00

frequency/degeneracy (CPFIT)
C2C.OOH: 100.3 (7.507); 1069.9 (12.133); 2730.8 (8.360)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12} = 1/2$ (OH + C=C). $E_{a,f}$ estimated the same 2.0 kcal mol^{-1} based on $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

IID. 27 CCyC.OC → C2.C=O

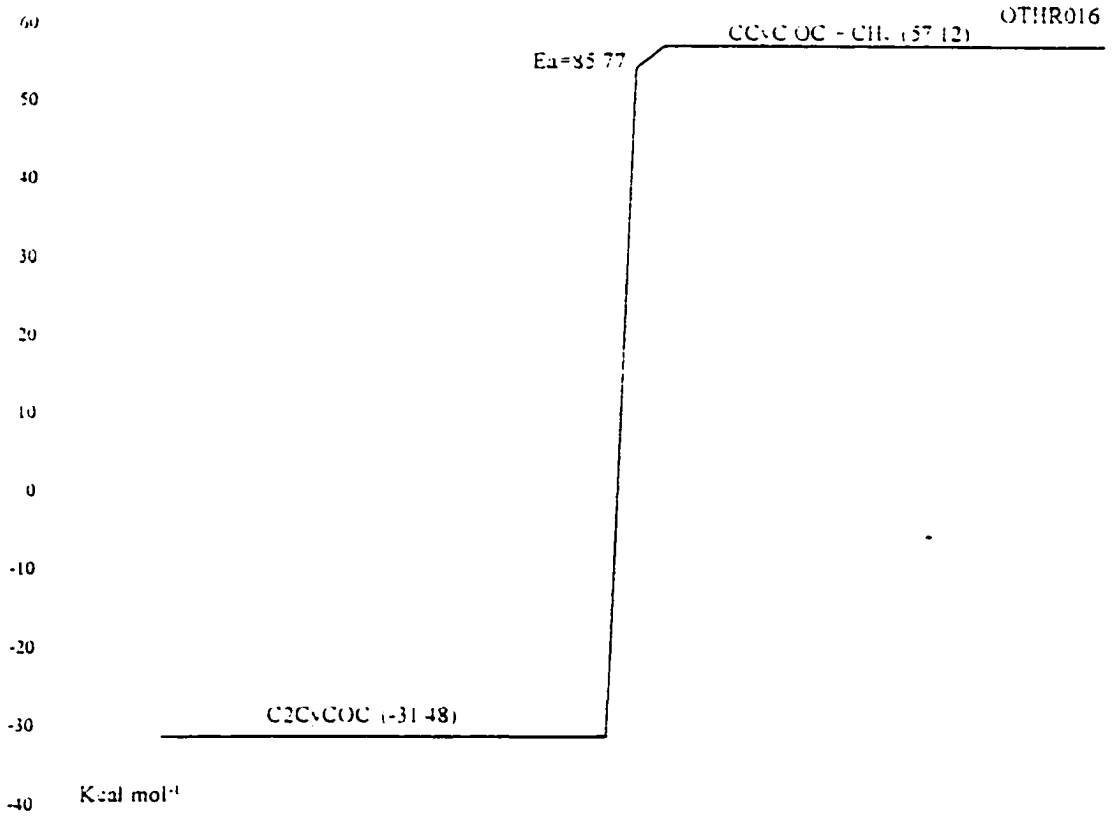


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CCyC.OC → C2.C=O	1.73×10^{13} $T^{1.0}$ e^{-0T}	3 89

frequency/degeneracy (CPFIT)
CCyC.OC: 250.1 (3.28); 1087.9 (11.744); 2928.9 (5.476)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f via A_r and Microscopic Reversbility (MR), A_r estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = -31.31 kcal mol^{-1}, $E_{a,r}$ estimated as ring strain difference plus considered addition to C=O double bond.

IID. 28 C2CyCOC → CCyC.OC + CH_3

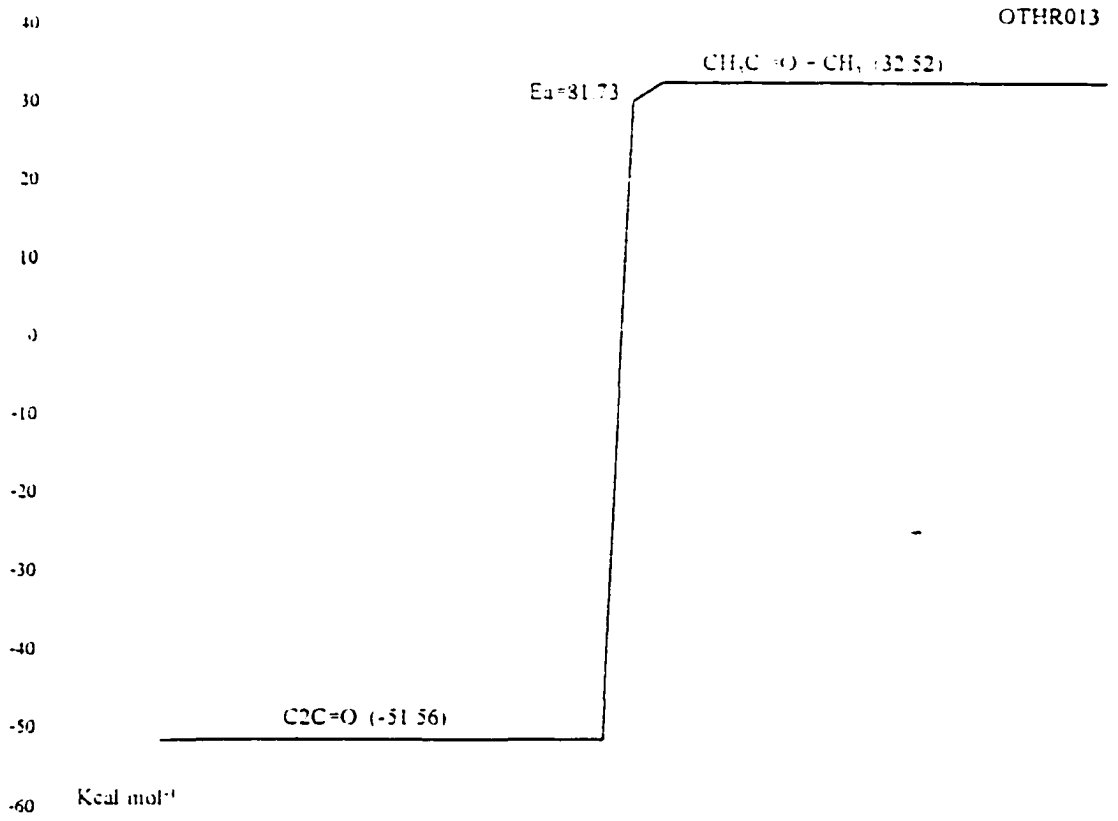


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2CyCOC → CCyC OC + CH_3	2.02×10^{17} T^0 e^{-0T}	85.77

frequency/degeneracy (CPFIT)
C2CyCOC: 469.6 (9.195) 1197.2 (15.095) 2986.5 (7.709)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.63 \times 10^{13}$, 90 TSA for C3C. + CH_3 → neo-C5. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 85.77 kcal mol^{-1}. $E_{a,r}$ = 0 kcal mol^{-1} (estimated by Bozzelli).

IID. 29 C2C=O → $CH_3C.=O$

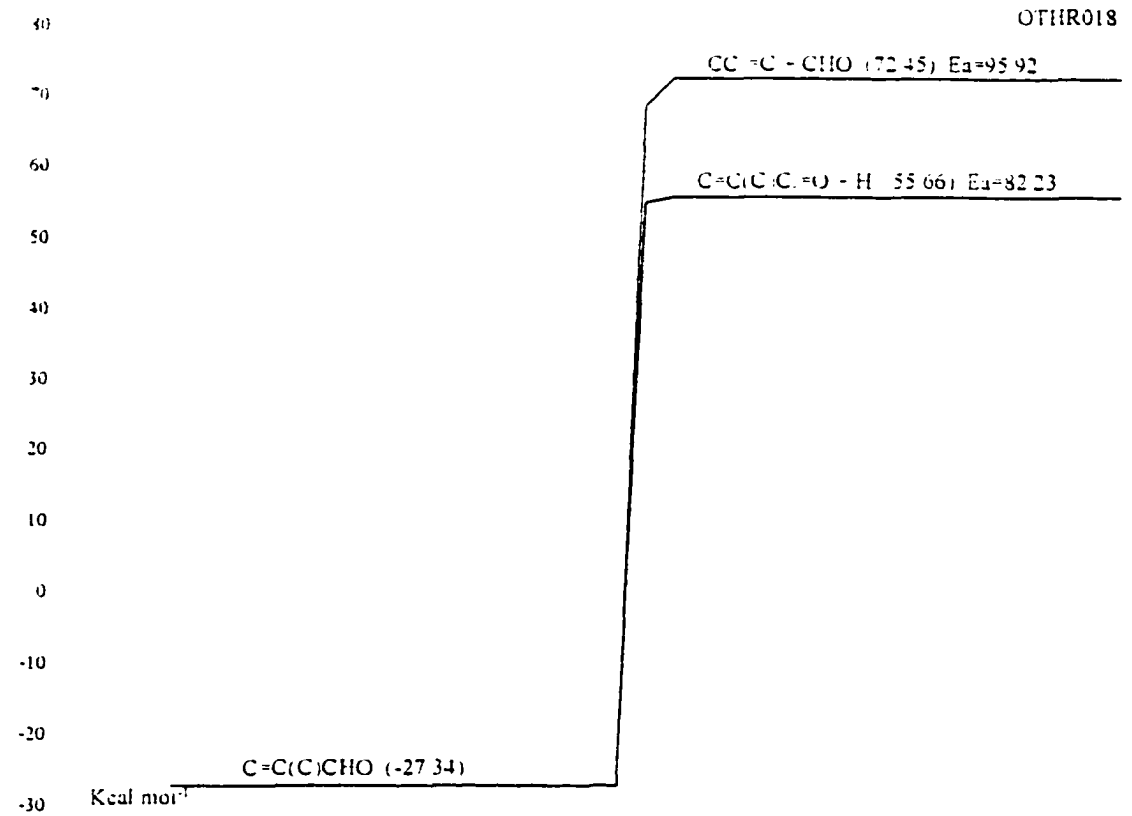


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C=O → $CH_3C.=O$	4.54×10^{18} $T^{-0.27}$ $e^{-0.00215T}$	81.73

frequency/degeneracy (CPFIT)
C2C=O: 478.2 (6.771); 1383.8 (10.063); 2760.1 (6.166)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 4.04 \times 10^{15}$ $T^{-0.8}$, 86 TSA. $E_{a,f}$ = ΔU_{rxn} = 81.73 kcal mol^{-1}.

IID. 30 C=C(C)CHO → Products



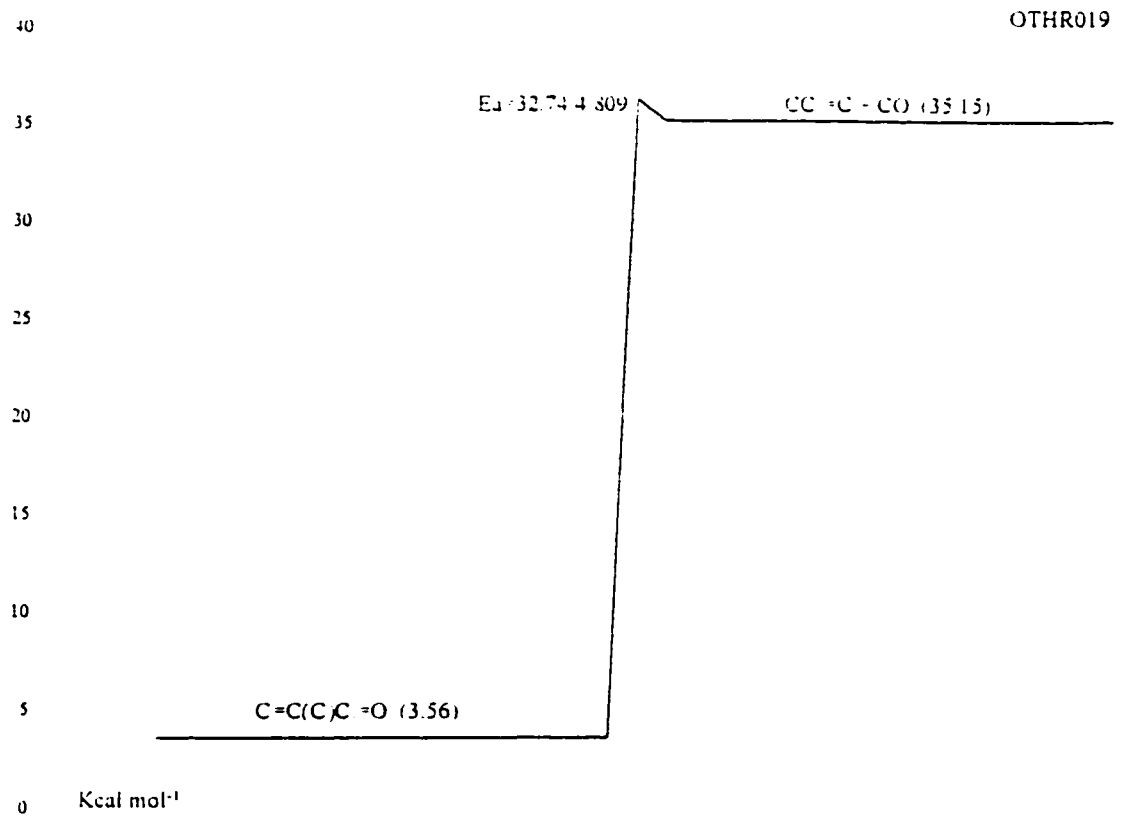
	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C=C(C)CHO → CCyC.OC + CH_2OOH	1.24×10^{17} T^0 e^{-0T}	95.92
k_2	C=C(C)CHO → CCyCOC(CO.) + OH	2.97×10^{14} T^0 e^{-0T}	82.23

frequency/degeneracy (CPFIT)
C=C(C)CHO: 425.2 (9.229); 1227.6 (10.817); 2929.6 (5.954)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, 88 TSA for CC.C + CHO → C2CCHO. $E_{a,f} = \Delta U_{rxn} = 95.92$ kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{13}$ 1/2 (H + CHO). $E_{a,f} = \Delta U_{rxn} = 82.23$ kcal mol^{-1}.

IID. 31 C=C(C)C.=O → CC.=C + CO



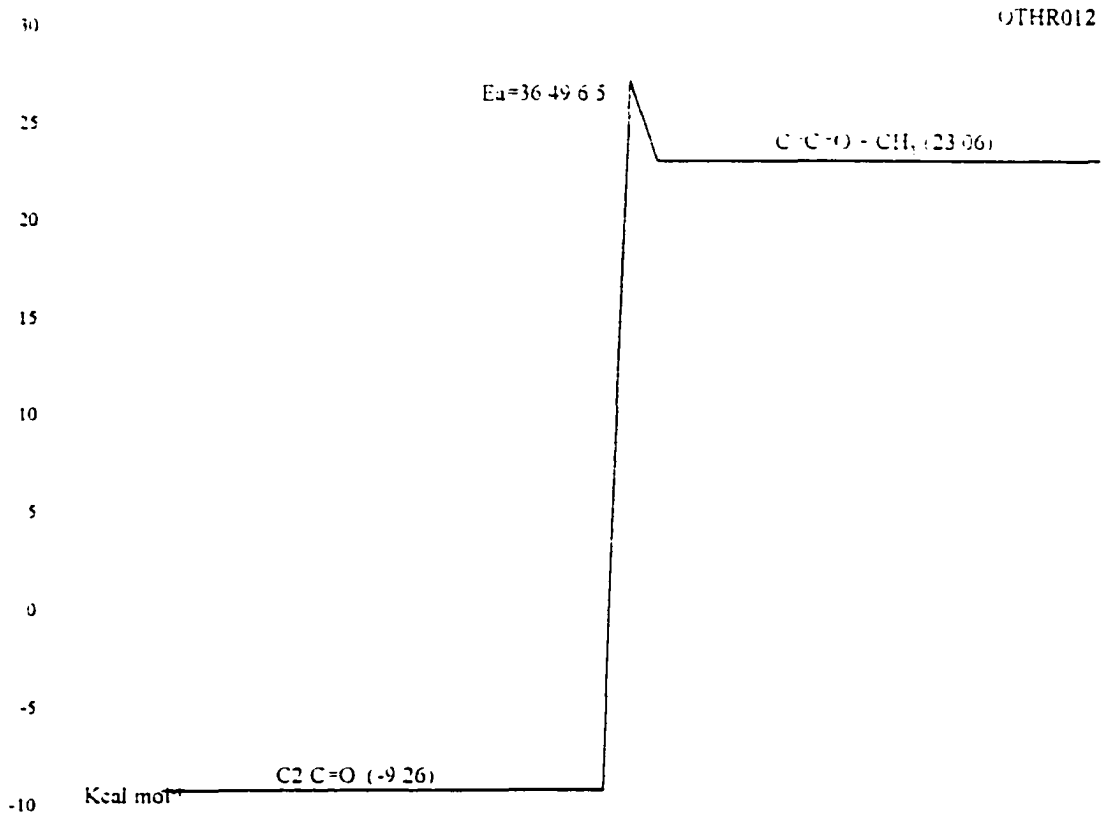
	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C=C(C)C.=O → CC.=C + CO	9.95×10^{13} T^0 e^{-0T}	32.74

frequency/degeneracy (CPFIT)
C=C(C)C.=O: 408.6 (9.006); 1183.9 (8.561); 2919.2 (5.433)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{11}$, 86 TSA for C=C. + CO → C=CC.=O. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 27.93 kcal mol^{-1}. $E_{a,r}$ = 4.809 kcal mol^{-1} (from the same reference as A_r)

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{13}$ 1/2 (H + CHO). $E_{a,f} = \Delta U_{rxn}$ = 82.23 kcal mol^{-1}.

IID. 32 C2.C=O → C=C=O + CH_3

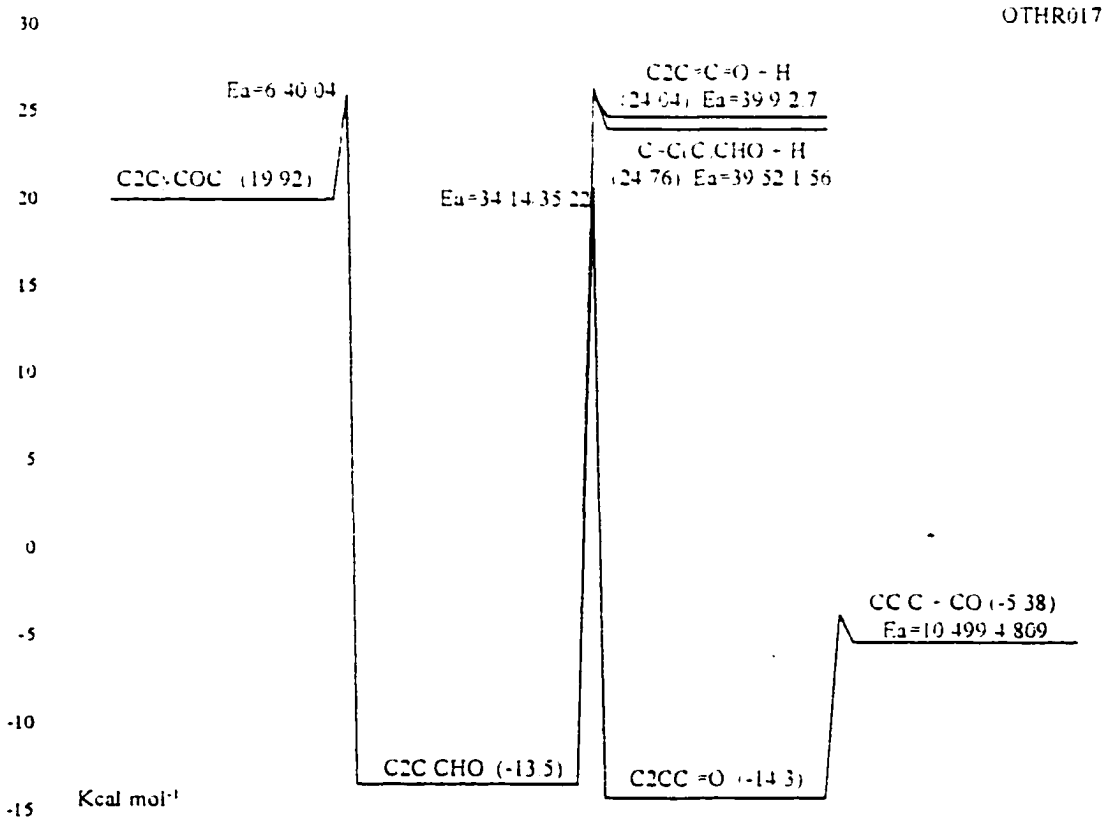


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2.C=O → C=C=O + CH_3	3.26×10^{12} T^0 e^{-0T}	36.49

frequency/degeneracy (CPFIT)
C2.C=O: 372.4 (5.286); 1158.0 (9.242); 2500.5 (5.471)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.58 \times 10^{11}$, 73 TSA2 for C=C=C + CH_3 → C2.C=C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 29.99 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1} (estimated by Bozzelli).

IID. 33 C2CyCOC. → C2C.CHO → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2CyCOC → C2C.CHO	1.71×10^{13} T^0 e^{-0T}	6 00
k_{-1}	C2C.CHO → C2CyCOC.	4.08×10^{12} T^0 e^{-0T}	40.04
k_2	C2C.CHO → C2C=C=O + H	1.40×10^{13} T^0 e^{-0T}	39.90
k_3	C2C.CHO → C=C(C)CHO + H	1.87×10^{13} T^0 e^{-0T}	39.52
k_4	C2C.CHO → C2CC.=O	6.50×10^{9} $T^{1.0}$ e^{-0T}	34.14
k_{-4}	C2CC.=O → C2C.CHO	7.34×10^{7} $T^{1.56}$ $e^{-0.00036T}$	35.22
k_5	C2CC.=O → CC.C + CO	1.77×10^{13} T^0 e^{-0T}	10.50

frequency/degeneracy (CPFIT)
C2CYCOC.: 432.8 (8.787); 1159.6 (13.398); 2960 2 (6.816)
C2C.CHO: 394.7 (9.643); 1273.2 (11.447); 2762.4 (7.410)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f}$ is estimated by Bozzelli (Chiungchu)

k_{-1} A_r estimated using TST, $A = (deg.)\ (ek_bT/h)\ \exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$?, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -34.04 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12}$ = 1/2 (H + CC=C → CC.C), 91 TSA/HAM. $E_{a,f}$ is estimated by Bozzelli.

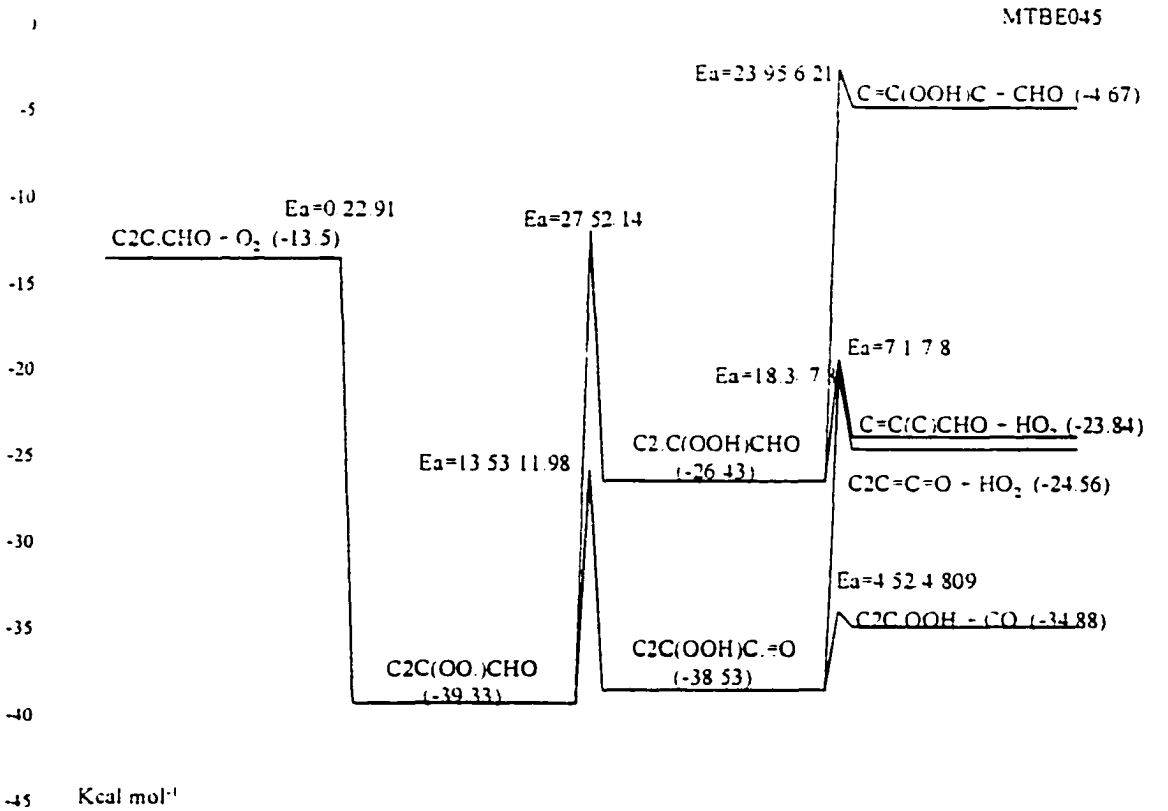
k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12}$ = 1/2 (H + CC=C → CC.C), 91 TSA/HAM. $E_{a,f}$ is estimated by Bozzelli.

k_4 A_r estimated using TST, $A = (deg.)\ (ek_b/h)\ T^n\ \exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f}$ = RS (28) + E_{abst} (6.14) kcal mol^{-1}.

k_{-4} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -1.08 kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{11}$, 86 TSA/HAM for CO + CC.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 5.69 kcal mol^{-1}. $E_{a,r}$ = 4.809 kcal mol^{-1}. (taken from the same reference as A_r).

IID. 34 C2C.CHO + O_2 → Products



	Reaction	A $T^n e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C.CHO + O_2 → C2C(OO.)CHO	1.81×10^{11} T^0 e^{-0T}	0.00
k_{-1}	C2C(OO.)CHO → C2C.CHO + O_2	5.66×10^{13} T^0 e^{-0T}	22.91
k_2	C2C(OO.)CHO → C2C(OOH)C.=O	1.49×10^{9} $T^{1.0}$ e^{-0T}	13.53
k_{-2}	C2C(OOH)C.=O → C2C(OO.)CHO	3.91×10^{11} $T^{-0.08}$ $e^{-0.0005T}$	11.98
k_3	C2C(OOH)C.=O → C2C=C=O + HO_2	4.86×10^{12} T^0 e^{-0T}	18.30
k_4	C2C(OOH)C.=O → C2C.OOH + CO	5.23×10^{13} T^0 e^{-0T}	4.52
k_5	C2C(OO.)CHO → C2.C(OOH)CHO	8.96×10^{9} $T^{1.0}$ e^{-0T}	27.52
k_{-5}	C2.C(OOH)CHO → C2C(OO.)CHO	3.11×10^{11} $T^{-0.09}$ $e^{-0.00063T}$	14.00
k_6	C2.C(OOH)CHO → C=C(C)CHO + HO_2	2.31×10^{12} T^0 e^{-0T}	7.10
k_7	C2.C(OOH)CHO → C=C(OOH)C + CHO	1.33×10^{13} T^0 e^{-0T}	23.95

frequency/degeneracy (CPFIT)
C2C(OO).CHO: 250.0 (9.921); 1062.4 (15.403); 2505.4 (8.676)
C2C(OOH)C.HO: 250.0 (10.700); 1079.7 (15.893); 2400.1 (6.907)

Lennard-Jones parameter
$\sigma(\text{Å}) = 5.86$, $\varepsilon/k\ (K) = 632.06$

k_1 92 WAL/AND, for C3C. + O_2.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = \Delta U_{rxn} = 22.91$ kcal mol^{-1}.

k_2 A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (5.98) + ΔU_{rxn} (1.55) kcal mol^{-1}

k_{-2} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, $\Delta U_{rxn} = 1.55$ kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.33 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 10.50$ kcal mol^{-1}. $E_{a,r} = 7.80$ kcal mol^{-1}. (estimated by Bozzelli).

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{11}$, 72 KER for C3C. + C#C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 0.29$ kcal mol^{-1}. $E_{a,r} = 4.809$ kcal mol^{-1}. (referenced on 88 TSA CC. + CO).

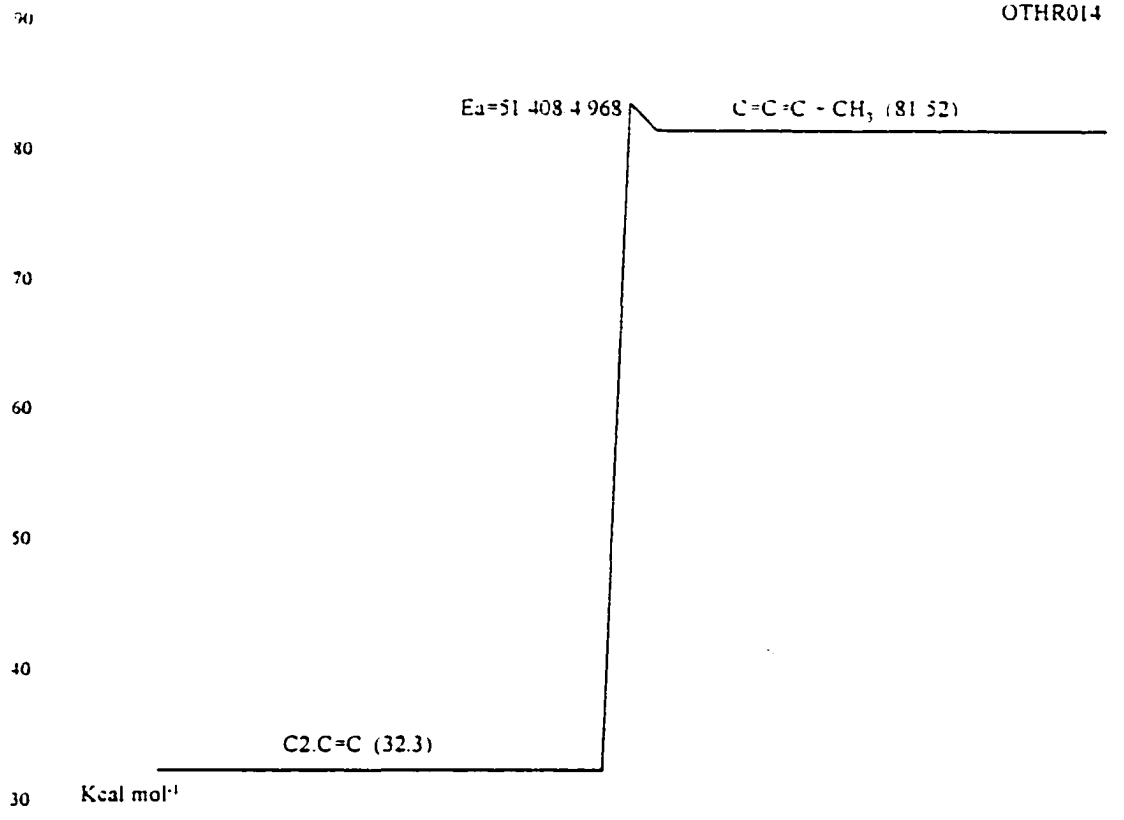
k_5 A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 6, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (8) + ΔU_{rxn} (13.52) kcal mol^{-1}

k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, $\Delta U_{rxn} = 13.52$ kcal mol^{-1}.

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.50 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = -0.71$ kcal mol^{-1}. $E_{a,r} = 7.80$ kcal mol^{-1}. (estimated by Bozzelli).

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.02 \times 10^{11}$, 86 LES/ROU for CHO + CC=C → Prod.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 17.74$ kcal mol^{-1}. $E_{a,r} = 6.21$ kcal mol^{-1}. (referenced as the same as the A_r).

IID. 35 C2.C=C → Products

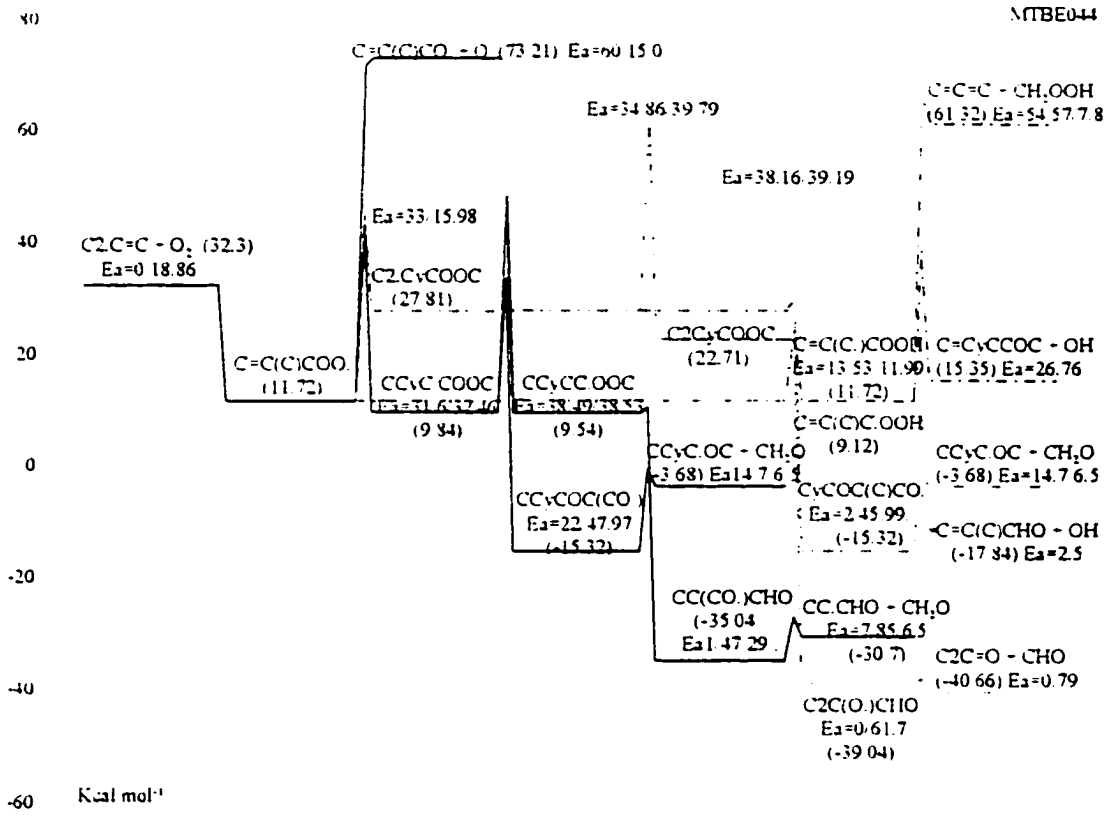


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2C.=C → C=C=C + CH_3	1.30×10^{13} T^0 e^{-0T}	51.41

frequency/degeneracy (CPFIT)
C2C.=C: 250.1 (4.454); 981.6 (12.636); 2533.9 (8.910)
Lennard-Jones parameter
σ(Å) = 5.18, ε/k (K) = 407.0

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.58 \times 10^{11}$, 73 TSA2. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 46.44 kcal mol^{-1}. $E_{a,r}$ = 4.968 kcal mol^{-1}. (taken from the same reference as A_r).

IID. 36 C2.C=C + O_2 → Products



	Reaction	A $T^n e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2.C=C + O_2 → C=C(C)COO.	5.00×10^{11} T^0 e^{-0T}	0.00
k_{-1}	C=C(C)COO. → C2.C=C + O_2	7.82×10^{12} T^0 e^{-0T}	18.86
k_2	C=C(C)COO. → C=C(C)CO. + O	1.84×10^{14} T^0 e^{-0T}	60 15
k_3	C=C(C)COO. → C=C(C)C.OOH	2.60×10^{10} $T^{1.0}$ e^{-0T}	37.95
k_{-3}	C=C(C)C.OOH → C=C(C)COO.	2.31×10^{13} $T^{0.18}$ $e^{-0.00007T}$	39.61
k_4	C=C(C)C.OOH → C=C(C)CHO + OH	1.23×10^{14} T^0 e^{-0T}	2.50
k_5	C=C(C)COO. → C=C(C.)COOH	5.15×10^{8} $T^{1.0}$ e^{-0T}	12.48
k_{-5}	C=C(C.)COOH → C=C(C)COO.	8.64×10^{12} $T^{-0.66}$ $e^{-0.00048T}$	11.00
k_6	C=C(C.)COOH → C=C=C + CH_2OOH	3.43×10^{13} T^0 e^{-0T}	54.57
k_7	C=C(C.)COOH → C=CyCCOC + OH	1.22×10^{12} $T^{-0.17}$ e^{-0T}	26.76
k_8	C=C(C)COO. → CCyC.COOC	4.68×10^{11} T^0 e^{-0T}	31.60
k_{-8}	CCyC.COOC → C=C(C)COO.	3.78×10^{13} T^0 e^{-0T}	31.96
k_9	CCyC.COOC → CCyCOC(CO.)	1.00×10^{13} T^0 e^{-0T}	22.00
k_{-9}	CCyCOC(CO.) → CCyC.COOC	6.85×10^{12} $T^{1.0}$ e^{-0T}	47.97
k_{10}	CCyCOC(CO.) → CCyC.OC + CH_2O	7.36×10^{13} T^0 e^{-0T}	14.70

	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_{11}	CCyC.COOC → CCyCC.OOC	2.26×10^{11} $T^{1.0}$ e^{-0T}	38.49
k_{-11}	CCyCC.OOC → CCyC.COOC	9.28×10^{12} $T^{0.46}$ $e^{-0.00034T}$	38.53
k_{12}	CCyCC.OOC → CC(CO.)CHO	5.20×10^{13} T^{0} e^{-0T}	1.00
k_{-12}	CC(CO.)CHO → CCyCC.OOC	4.68×10^{11} T^{0} e^{-0T}	47.29
k_{13}	CC(CO.)CHO → CC.CHO + CH_2O	1.73×10^{12} T^{0} e^{-0T}	7.85
k_{14}	C=C(C)COO. → C2.CyCOOC	4.68×10^{11} T^{0} e^{-0T}	33.00
k_{-14}	C2.CyCOOC → C=C(C)COO.	2.02×10^{13} T^{0} e^{-0T}	15.33
k_{15}	C2.CyCOOC → CCyCOC(CO.)	4.08×10^{12} T^{0} e^{-0T}	2.00
k_{-15}	CCyCOC(CO.) → C2.CyCOOC	5.23×10^{12} T^{0} e^{-0T}	45.99
k_{16}	CCyCOC(CO.) → C2C(OOH)CO.	7.36×10^{13} T^{0} e^{-0T}	14.70
k_{17}	C2.CyCOOC → C2CyCOOC.	1.30×10^{10} $T^{1.0}$ e^{-0T}	34.86
k_{-17}	C2CyCOOC. → C2.CyCOOC	1.14×10^{12} $T^{0.46}$ $e^{-0.00042T}$	39.79
k_{18}	C2CyCOOC. → C2C(O.)CHO	4.78×10^{13} T^{0} e^{-0T}	0.00
k_{-18}	C2C(O.)CHO → C2CyCOOC.	4.08×10^{12} T^{0} e^{-0T}	62.70
k_{19}	C2C(O.)CHO → C2C=O + CHO	2.20×10^{13} T^{0} e^{-0T}	0.79

frequency/degeneracy (CPFIT)
C=C(C)COO.: 250.2 (9.328); 1085.2 (12.518); 2775.4 (9.654)
C=C(C)C.OOH: 250.1 (9.281); 1072.2 (13.818); 2573.4 (7.901)
C=C(C.)COOH: 250.1 (9.354); 1014.6 (14.110); 2587.6 (7.537)
CCyC.COOC: 250.2 (5.838); 1079.1 (19.700); 2566.7 (6.963)
C2.CyCOOC: 250.2 (5.146); 955.4 (18.106); 2284.9 (8.748)
CCyCOC(CO.): 479.0 (11.457); 1251.1 (14.140); 3091.0 (6.403)
CCyCC.OOC: 250.1 (5.427); 1047.2 (20.847); 2766.5 (6.227)
C2CyCOOC.: 250.6 (5.473); 961.6 (18.784); 2467.2 (7.743)
CC(CO.)CHO: 392.3 (10.257); 1270.1 (14.560); 2975.3 (6.683)
C2C(O.)CHO: 431.6 (12.207); 1412.1 (15.266); 3486.6 (4.027)
Lennard-Jones parameter
σ(Å) = 5.86, ε/k (K) = 632.06

k_1 1/2(C3C. + O_2 → C3COO.), 88 XI

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -18.86 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for ($CH_3O$ + O → Prod.. $E_{a,f} = \Delta U_{rxn}$ = 60.15 kcal mol^{-1}.

k_3 A_f estimated using TST, A = (deg.) A′ T^n, deg. = 2, A′ = 1.011×10^9, n = 1.455, A′ and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (26) + E_{abst} (12.16) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -1.03 kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12} = 1/2$ (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_5 A_f estimated using TST, A = (deg.) A' T^n, deg. = 3, A' = 1.275×10^6, n = 1.954, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ = RS (0) + E_{abst} (11.97) + ΔH_{rxn} (1.54) kcal mol^{-1}.

k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 1.54 kcal mol^{-1}.

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for $C_3H_6 + CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 46.77 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_7 A_f estimated using TST, A = (deg.) A' T^n, deg. = 1, A' = 1.216×10^{12}, n = -0.173, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ is estimated by Bozzelli (Chiungchu).

k_8 A_f estimated using TST, A = (deg.) A' T^n, deg. = 1, A' = 4.090×10^8, n = 0.923, A' and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ is estimated by Bozzelli (Chiungchu).

k_{-8} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -0.86 kcal mol^{-1}.

k_9 A_f is taken from ref. [55] $E_{a,f}$ is estimated as the difference of ring strain (28 - 6) kcal mol^{-1}. (estimated by Bozzelli).

k_{-9} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -25.97 kcal mol^{-1}.

k_{10} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.08 \times 10^{11}$, 88 TSA for CH_2O + CC.C $\rightarrow$ CCC + CHO. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 8.2 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (estimated by Bozzelli).

k_{11} A_r estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 4, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of rotor (no rotor loss here, thus $\Delta S^{\neq}(T) = 0$). $E_{a,f}$ = RS (28) + E_{abst} (10.49) kcal mol^{-1}.

k_{-11} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -0.04 kcal mol^{-1}.

k_{12} A_f via A_r and Microscopic Reversbility (MR), $E_{a,f}$ is estimated as 1 kcal mol^{-1} by Bozzelli.

k_{-12} A_r estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -46.29 kcal mol^{-1}.

k_{13} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.08 \times 10^{11}$, 88 TSA for CH_2O + CC.C $\rightarrow$ CCC + CHO. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 1.35 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (estimated by Bozzelli).

k_{14} A_f estimated using TST, A = (deg.) A' T^n, deg. = 1, A' = 1.222×10^9, n = 0.99, A'

and n are from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f}$ is estimated as difference of ring strain plus 7 kcal mol^{-1} for addition to C=C double bond.

k_{-14} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 17.02 kcal mol^{-1}.

k_{15} A_f estimated using TST, $A = (deg.)\ (ek_bT/h)\ \exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f}$ is estimated by Bozzelli.

k_{-15} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -43.99 kcal mol^{-1}.

k_{16} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.08 \times 10^{11}$, 88 TSA for CH_2O + CC.C → CCC + CHO. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 8.2 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (estimated by Bozzelli).

k_{17} A_r estimated using TST, $A = (deg.)\ (ek_b/h)\ T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 2, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f}$ = RS (26) + E_{abst} (8.86) kcal mol^{-1}.

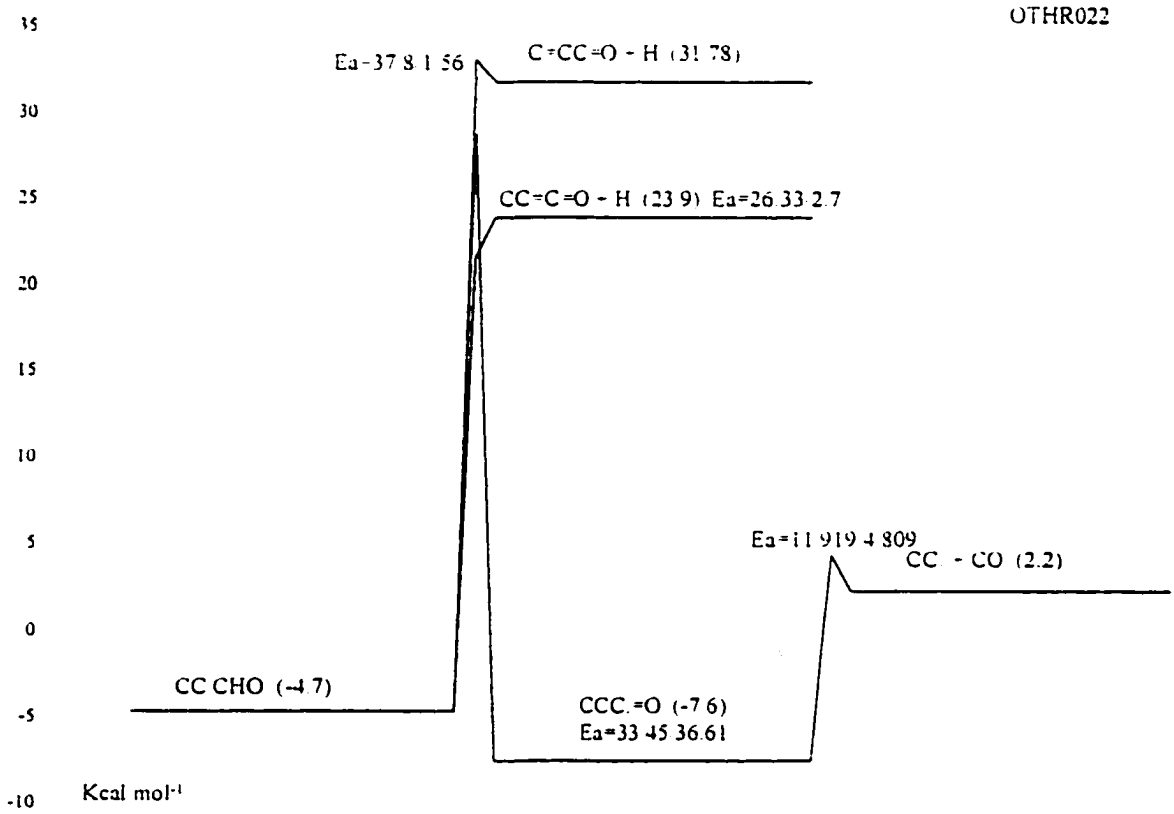
k_{-17} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -4.93 kcal mol^{-1}.

k_{18} A_f via A_r and Microscopic Reversbility (MR), $E_{a,f}$ is estimated as 0 kcal mol^{-1} by Bozzelli.

k_{-18} A_r estimated using TST, $A = (deg.)\ (ek_bT/h)\ \exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$, $\Delta S^{\neq}(T)$ is estimated as loss of one rotors (-4.3 cal mol^{-1} K^{-1}). $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -62.7 kcal mol^{-1}.

k_{19} A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.10 \times 10^{10}$ =1/2 (CC=C + CHO → Prod.), 86 LES/ROU. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = -5.71 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (estimated by Bozzelli).

IID. 37 CC.CHO → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC.CHO → CCC.=O	6.50×10^{9} $T^{1.0}$ e^{-0T}	33.45
k_{-1}	CCC.=O → CC.CHO	9.86×10^{8} $T^{1.0}$ $e^{-0.00023T}$	36.61
k_2	CCC.=O → CC. + CO	8.14×10^{12} T^{0} e^{-0T}	11.92
k_3	CC.CHO → C=CCHO + H	2.58×10^{13} T^{0} e^{-0T}	37.80
k_4	CC.CHO → CC=C=O + H	2.96×10^{10} T^{0} e^{-0T}	26.33

frequency/degeneracy (CPFIT)
CC.CHO: 433.2 (6.147); 1255.8 (8.449); 2726.7 (5.404)
CCC.=O: 518.7 (8.551); 1777.1 (8.864); 3567.0 (2.585)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_r estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}).

$E_{a,f}$ = RS (28) + E_{abst} (5.45) kcal mol^{-1}.

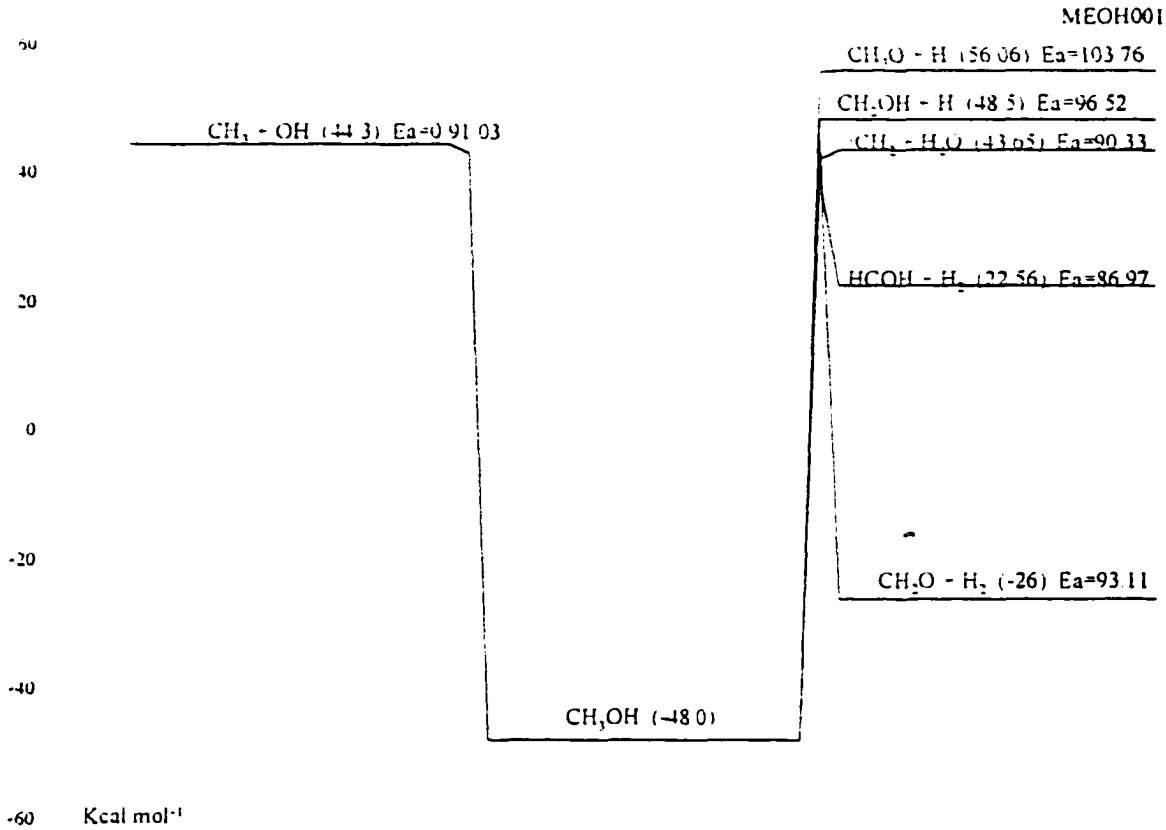
k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -3.16 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{11}$, 86 TSA/HAM for CO + CC $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 7.11 kcal mol^{-1} $E_{a,r}$ = 4.809 kcal mol^{-1}. (taken from the same reference as A_r).

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 7.42 \times 10^{12}$, 72 KER for C=C + H. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 36.24 kcal mol^{-1}. $E_{a,r}$ = 1.56 kcal mol^{-1}. (taken from the same reference as A_r).

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12}$ = 1/2 (H + CC=C → CC.C), 91 TSA/HAM. $E_{a,f}$ is estimated by Bozzelli.

IID. 38 $CH_3OH \rightarrow$ Products



	Reaction	A $T^n e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$CH_3OH \rightarrow CH_2O + H_2$	$3.02\times10^{9}\ T^{1.29}\ e^{-0T}$	93.11
k_2	$CH_3OH \rightarrow {}^1HCOH + H_2$	$1.09\times10^{14}\ T^{0}\ e^{-0T}$	86.97
k_3	$CH_3OH \rightarrow {}^1CH_2 + H_2O$	$4.40\times10^{14}\ T^{0}\ e^{-0T}$	90.33
k_4	$CH_3OH \rightarrow CH_3 + OH$	$5.60\times10^{15}\ T^{0}\ e^{-0T}$	91.03
k_5	$CH_3OH \rightarrow CH_2OH + H$	$1.55\times10^{15}\ T^{0}\ e^{-0T}$	96.52
k_6	$CH_3OH \rightarrow CH_3O + H$	$1.39\times10^{14}\ T^{0}\ e^{-0T}$	103.76

frequency/degeneracy (CPFIT)
CH_3OH: 753.6 (3.317); 1827.7 (6.176); 3999.9 (2.006)
Lennard-Jones parameter
σ(Å) = 3.76, ε/k (K) = 369.16

k_1 A_f is from AFACT2f thermodynamic analysis with thermodynamic properties calculated by MOPAC PM3, $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (21.11) kcal-mol^{-1}, $E_{a,r}$ is estimated

as 72.0 kcal-mol^{-1} based on reference Walch (1993) [95].

k_2 A_f is taken from Bozzelli (1991) [21]. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (70.43) kcal-mol^{-1}, $E_{a,r}$ is estimated as 16.54 kcal-mol^{-1} based on reference Walch (1993) [95].

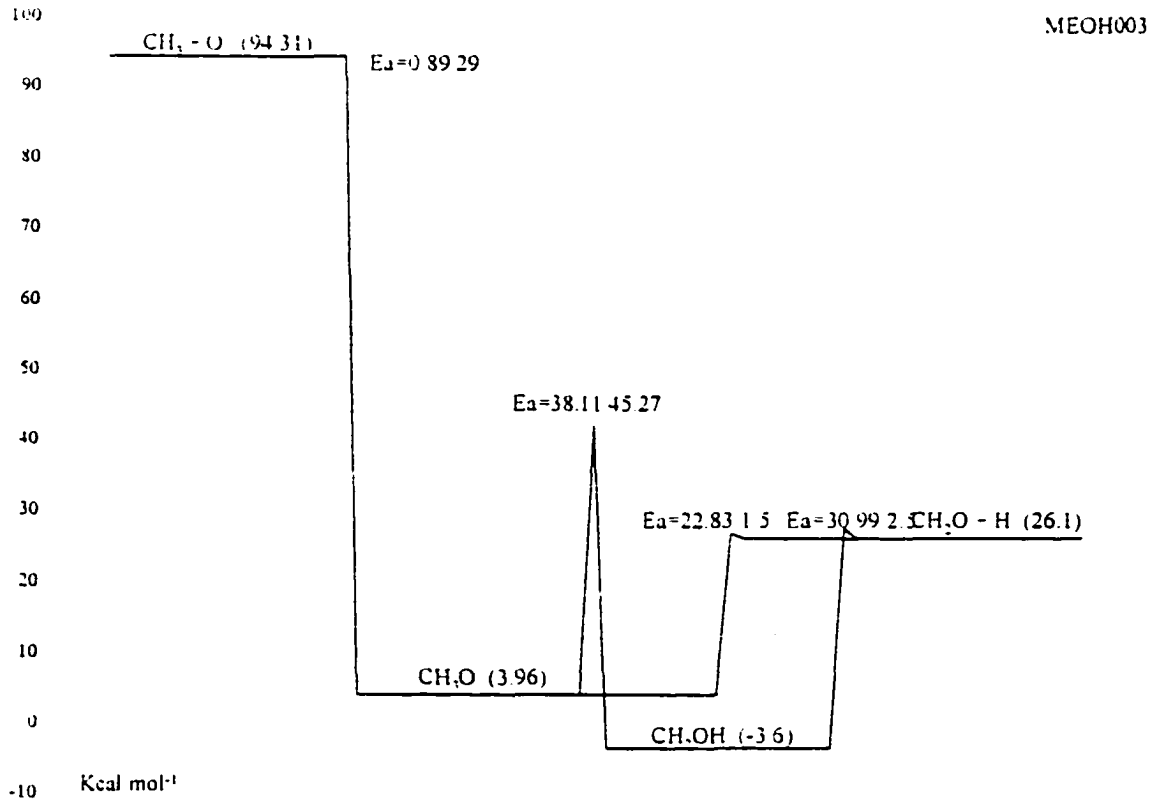
k_3 A_f is taken from Bozzelli (1991) [21]. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (90.33) kcal-mol^{-1}, $E_{a,r}$ is estimated as 0 kcal-mol^{-1} based on reference Walch (1993) [95].

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.61 \times 10^{13}$, 92 BAU/COB, NIST, $E_{a,f} = \Delta U_{rxn} = 91.03$ kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.00 \times 10^{13}$, 81 HOY/COF, $E_{a,f} = \Delta U_{rxn} = 96.52$ kcal mol^{-1}.

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.00 \times 10^{13}$, 91 DOB/BER, $E_{a,f} = \Delta U_{rxn} = 103.76$ kcal mol^{-1}.

IID. 39 $CH_3O/CH_2OH \rightarrow$ Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$CH_3 + O \rightarrow CH_3O$	7.83×10^{13} T^0 e^{-0T}	0.00
k_{-1}	$CH_3O \rightarrow CH_3 + O$	2.97×10^{15} T^0 e^{-0T}	89.29
k_2	$CH_3O \rightarrow CH_2O + H$	1.55×10^{13} T^0 e^{-0T}	22.83
k_3	$CH_3O \rightarrow CH_2OH$	1.71×10^{11} $T^{1.0}$ e^{-0T}	38.11
k_{-3}	$CH_2OH \rightarrow CH_3O$	2.37×10^{14} $T^{-0.72}$ $e^{-0.00015T}$	45.27
k_6	$CH_2OH \rightarrow CH_2O + H$	1.16×10^{12} T^0 e^{-0T}	30.99

frequency/degeneracy (CPFIT)
CH_3O: 1189.6 (4.569); 2053.5 (3.381); 3999.3 (1.050)
Lennard-Jones parameter
σ(Å) = 3.76, ε/k (K) = 369.16

k_1 86 TSA/HAM

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 89.29 kcal

mol^{-1}.

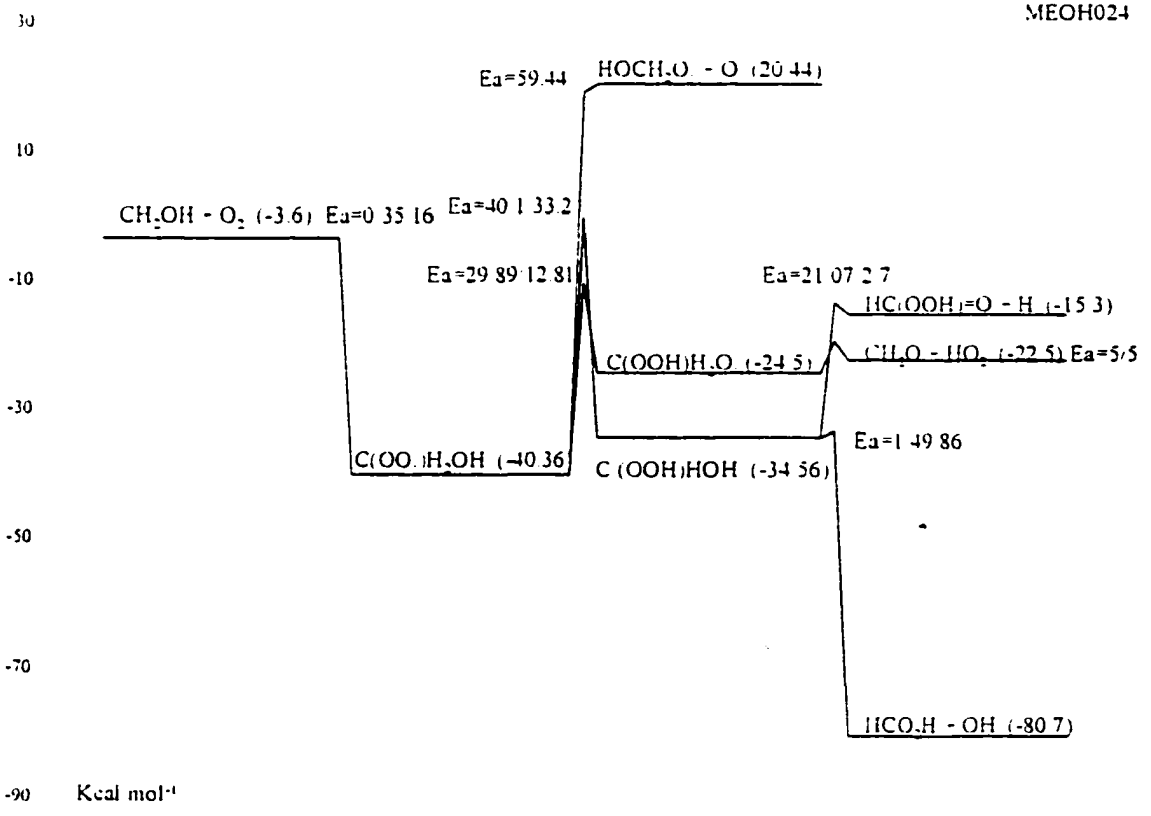
k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{13}$, 84 WAR for H + CH_2O. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 21.33$ kcal mol^{-1}. $E_{a,r} = 1.50$ kcal mol^{-1} (from the same reference as A_r)

k_3 A_f estimated using TST, $A = (deg.)\,(ek_b/h)\exp(\Delta S^{\ddagger}(T)/R)\,T^n$, deg. = 3, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\ddagger}(T)$ is estimated as loss of rotor (no rotor lost here, so $\Delta S^{\ddagger}(T)$ is 0 kcal mol^{-1}). $E_{a,f}$ = RS (28) + E_{abst} (10.11) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -7.16 kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{13}$, 84 WAR for H + CH_2O. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 21.33$ kcal mol^{-1}. $E_{a,r} = 2.50$ kcal mol^{-1} (estimated by Bozzelli)

IID. 40 $CH_2OH + O_2 \rightarrow$ Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$CH_2OH + O_2 \rightarrow C(OO.)H_2OH$	6.00×10^{12} T^0 e^{-0T}	0.00
k_1	$C(OO.)H_2OH \rightarrow CH_2OH + O_2$	2.75×10^{14} T^0 e^{-0T}	35.16
k_2	$C(OO.)H_2OH \rightarrow HOCH_2O.$	1.23×10^{14} T^0 e^{-0T}	59.44
k_3	$C(OO.)H_2OH \rightarrow C(OOH)H_2O.$	1.49×10^{9} $T^{1.0}$ e^{-0T}	29.89
k_{-3}	$C(OOH)H_2O. \rightarrow C(OO.)H_2OH$	2.54×10^{12} $T^{-0.15}$ $e^{-0.00016T}$	12.81
k_4	$C(OOH)H_2O. \rightarrow C(OO.)H_2OH$	4.10×10^{12} T^0 e^{-0T}	5.00
k_5	$C(OO.)H_2OH \rightarrow HOC.HOOH$	2.60×10^{10} $T^{1.0}$ e^{-0T}	40.10
k_{-5}	$HOC.HOOH \rightarrow C(OO.)H_2OH$	3.79×10^{14} $T^{-0.78}$ $e^{-0.00093T}$	33.20
k_6	$HOC.HOOH \rightarrow HCO2H + OH$	3.80×10^{13} T^0 e^{-0T}	1.00
k_7	$HOC.HOOH \rightarrow HOOCHO + H$	1.48×10^{13} T^0 e^{-0T}	21.07

frequency/degeneracy (CPFIT)

$C(OO.)H_2OH$: 250.5 (4.365); 1024.3 (3.133); 2314.0 (6.502)

$C(OOH)H_2O.$: 257.7 (4.476); 801.4 (3.128); 1871.3 (6.396)

HOC.HOOH: 100.1 (3.079); 580.9 (4.827); 2001.8 (5.594)

Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 2 × (CC. + O_2), 90 DEM/SAN and 89 ATK/BAU.

k_1 A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f}(0) - \Delta U_{rxn}$ (-35.16) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for $O + CH_3O \rightarrow$ Prod.. $E_{a,f} = E_{a,r}(0) + \Delta U_{rxn}$ (59.44) kcal mol^{-1}.

k_3 A_f estimated using TST, A = (deg.) (ek_b/h) $\exp(\Delta S^{\neq}(T)/R)$ T^n, deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 kcal mol^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (6.81) + ΔH_{rxn} (17.08) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (17.08) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.01 \times 10^{11}$, 72 KER/PAR for $C{=}C + HO_2 \rightarrow$ Prod.. $E_{a,f}$ is estimated by Bozzelli.

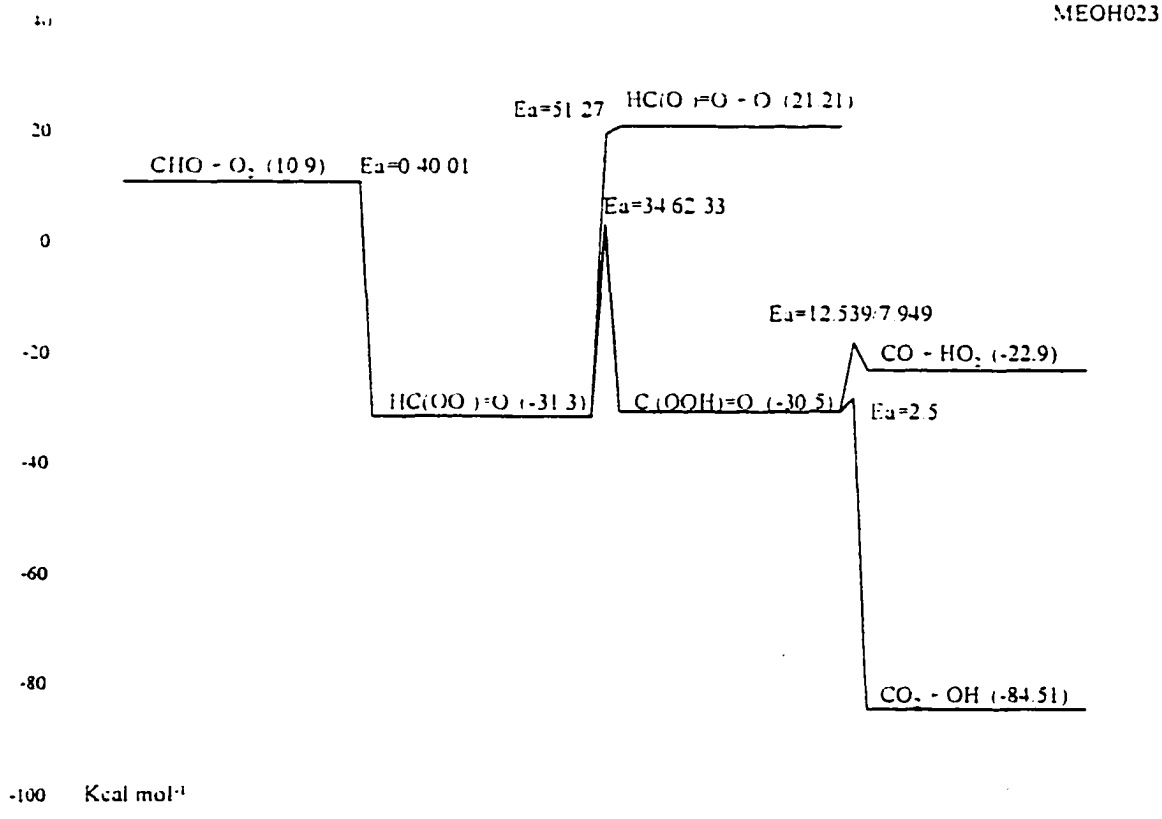
k_5 A_f estimated using TST, A = (deg.) (ek_b/h) $\exp(\Delta S^{\neq}(T)/R)$ T^n, deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 kcal mol^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (7.20) + ΔH_{rxn} (6.90) kcal mol^{-1}.

k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (6.90) kcal mol^{-1}.

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 1.0 kcal mol^{-1} based on $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{13}$, 84 WAR for H + CH_2O. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (18.37) kcal mol^{-1}. $E_{a,r}$ = 2.7 kcal mol^{-1} (estimated by Bozzelli)

IID. 41 CHO + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	CHO + O_2 → HC(OO.)=O	6.00×10^{12} T^0 e^{-0T}	0.00
k_{-1}	HC(OO.)=O → CHO + O_2	3.95×10^{13} T^0 e^{-0T}	40.01
k_2	HC(OO.)=O → HC(O.)=O + O	2.98×10^{14} T^0 e^{-0T}	51.27
k_3	HC(OO.)=O → C.(OOH)=O	1.30×10^{10} $T^{1.0}$ e^{-0T}	34.62
k_{-3}	C.(OOH)=O → HC(OO.)=O	1.13×10^{13} $T^{-0.29}$ $e^{-0.00066T}$	33.00
k_4	C.(OOH)=O → CO + HO_2	2.33×10^{11} T^0 e^{-0T}	12.54
k_5	C.(OOH)=O → CO_2 + OH	2.10×10^{11} T^0 e^{-0T}	1.50

frequency/degeneracy (CPFIT)
HC(OO.)=O: 396.2 (2.750); 802.3 (1.921); 2085.1 (3.828)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f is taken as 2 times 90 DEM/ASN & 89 ATK/BAU for CC. + O_2. $E_{a,f}$ is 0 from

the same reference.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -40.01 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for $O + CH_3O \rightarrow$ Prod.. $E_{a,f} = \Delta U_{rxn}$ = 51.27 kcal mol^{-1}.

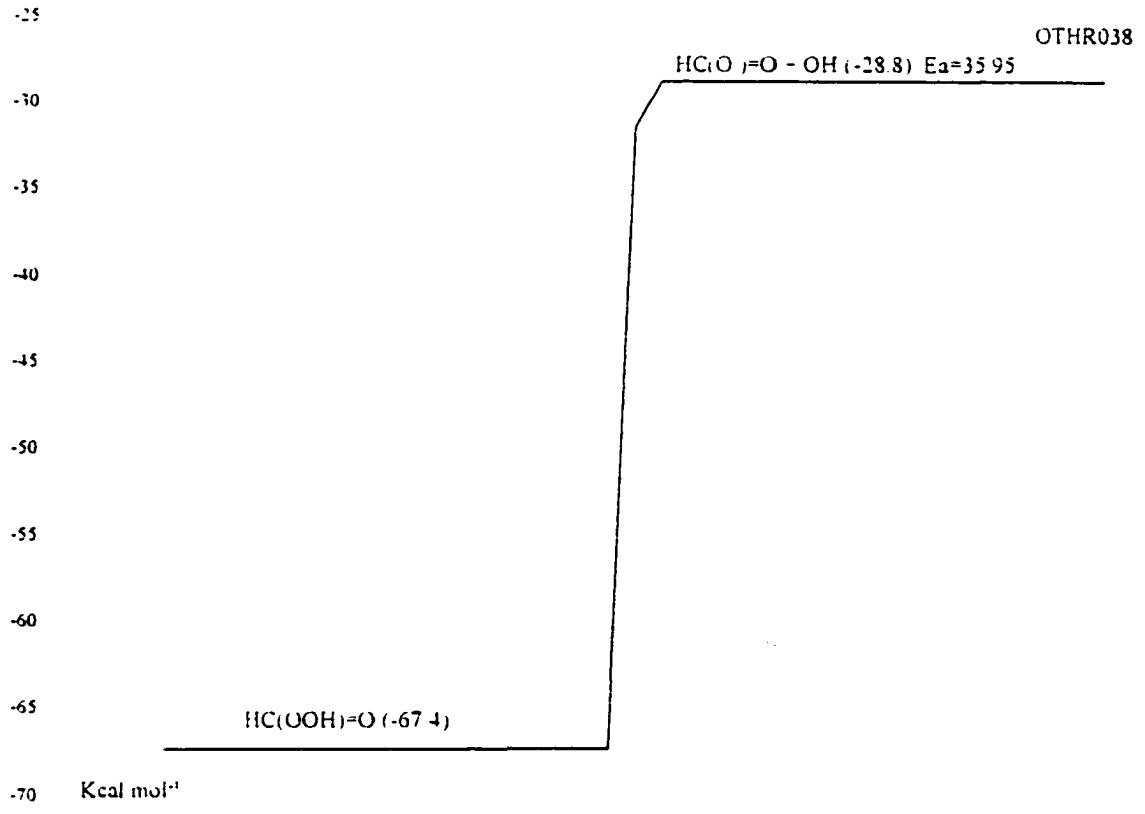
k_3 A_f estimated using TST, A = (deg.) (ek_b/h) $\exp(\Delta S^{\ddagger}(T)/R)$ T^n, deg. = 3, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\ddagger}(T)$ is estimated as loss of one rotor (-4.3 kcal mol^{-1}) and gain one optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (7) + ΔU_{rxn} (1.62) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 1.62 kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.21 \times 10^{11}$, 86 TSA/HAM for $C_2H_2 + CH_3O \rightarrow$ Prod.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 4.59 kcal mol^{-1}. $E_{a,r}$ = 7.949 kcal mol^{-1} (referenced from 86 TSA for $C_2H_2 + HO_2 \rightarrow CH_2CO + OH$)

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 1.5 kcal mol^{-1} based on $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

IID. 42 HC(OOH)=O → HC(O.)=O + OH

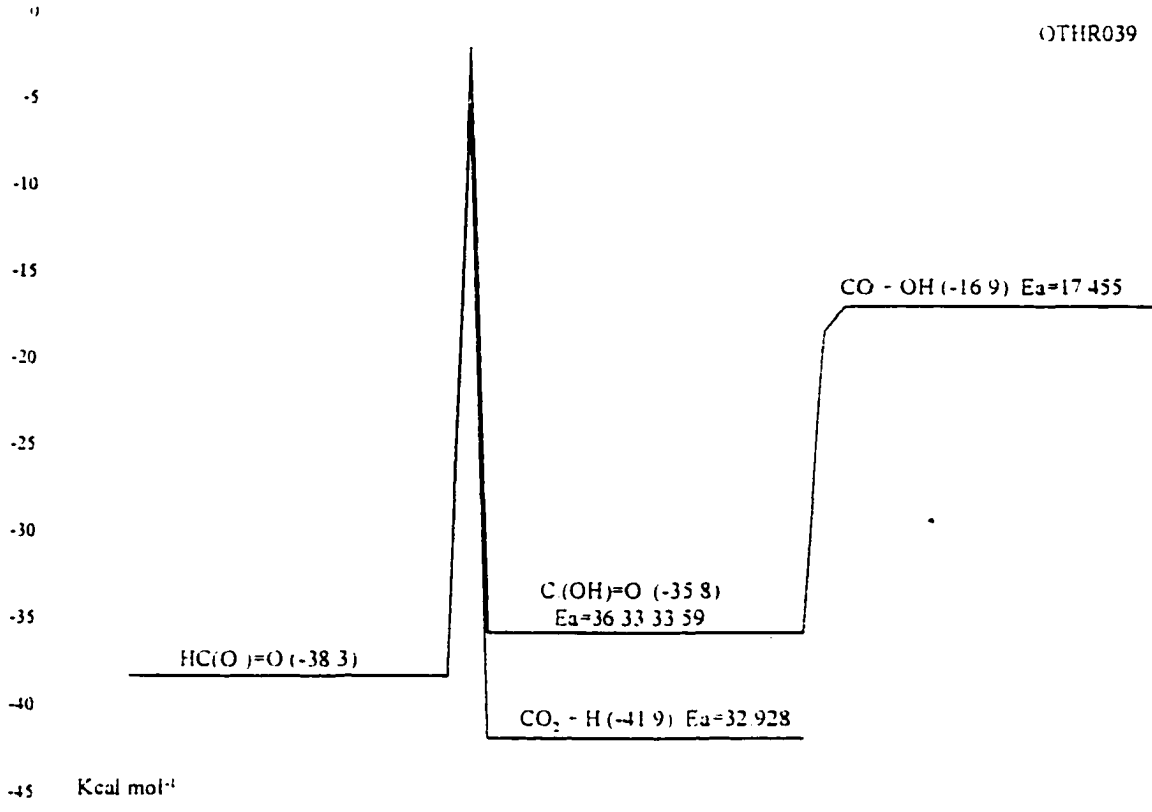


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	HC(OOH)=O → HC(O.)=O + OH	2.20×10^{15} T^0 e^{-0T}	35.95

frequency/degeneracy (CPFIT)
HC(OOH)=O: 425.5 (3.716); 800.4 (2.821); 1723.9 (4.464)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 91 TSA/HAM for C=CC. + OH. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (35.95) kcal mol^{-1}.

IID. 43 HC(O.)=O → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	HC(O.)=O → CO_2 + H	1.74×10^{12} $T^{0.31}$ e^{-0T}	32.93
k_2	HC(O.)=O → C.(OH)=O	5.66×10^{10} $T^{1.0}$ e^{-0T}	36.33
k_{-2}	C.(OH)=O → HC(O.)=O	3.15×10^{12} $T^{0.16}$ $e^{-0.00069T}$	33.59
k_3	C.(OH)=O → CO + OH	4.11×10^{11} T^{0} e^{-0T}	17.46

frequency/degeneracy (CPFIT)
HC(O.)=O: 962.8 (1.855); 954.9 (1.796); 2215.5 (2.349)
C.(OH)=O: 500.5 (1.780); 800.0 (1.194); 1777.2 (2.525)
Lennard-Jones parameter
σ(Å) = 4.35, ε/k (K) = 422.61

k_1* 88 LAR/STE.

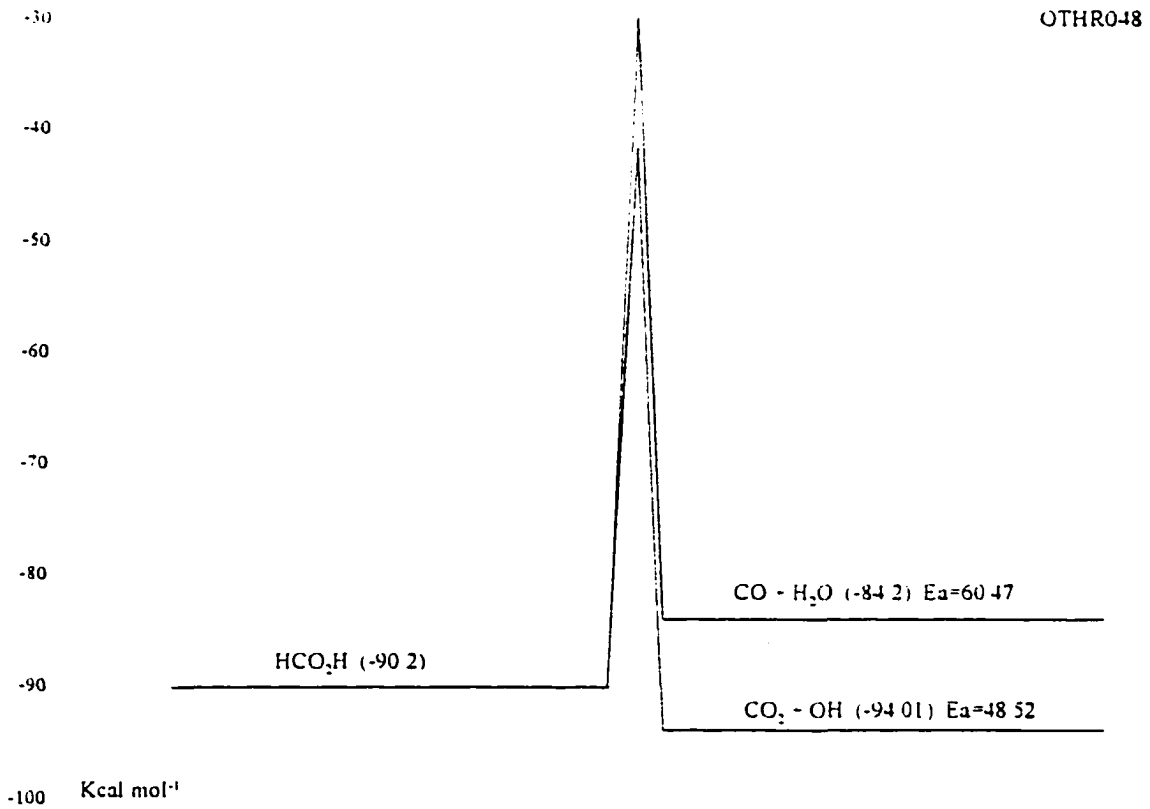
k_2 A_f estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}(T)/R$), deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of rotor (no rotor loss here, so

$\Delta S^{\neq}(T) = 0)$, $E_{a,f} = RS\ (28) - E_{abs}\ (5\ 59)$ kcal mol^{-1}.

k_{-2} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}\ (-25.0) + \Delta H_{rxn}$ (2.74) kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3\ 09 \times 10^{11}$, 72 DIX for CO + OH $\rightarrow$ CO_2 + H, $E_{a,f} = E_{a,r}\ (0\ 735) + \Delta U_{rxn}\ (16\ 72)$ kcal mol^{-1}.

IID. 44 $HCO_2H \rightarrow$ Products

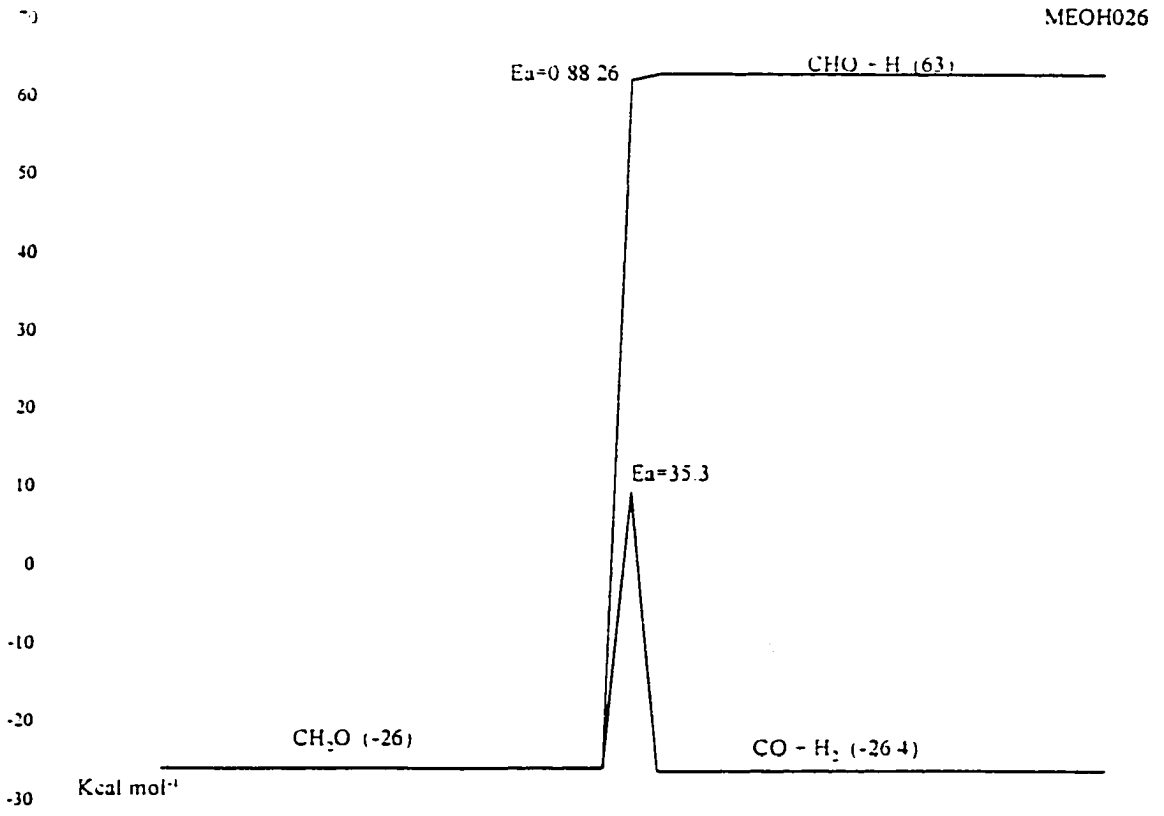


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$HCO_2H \rightarrow CO + H_2O$	2.45×10^{12} T^0 e^{-0T}	60.47
k_2	$HCO_2H \rightarrow CO_2 + H_2$	2.95×10^{9} T^0 e^{-0T}	48.52

frequency/degeneracy (CPFIT)
HCO_2H: 747.0 (2.569); 996.2 (2.452); 2148.2 (3.479)
Lennard-Jones parameter
σ(Å) = 4.34, ε/k (K) = 422.61

k_1 71 BLA/DAL, NIST
k_2 71 BLA/DAL, NIST

IID. 45 $CH_2O \rightarrow$ Products

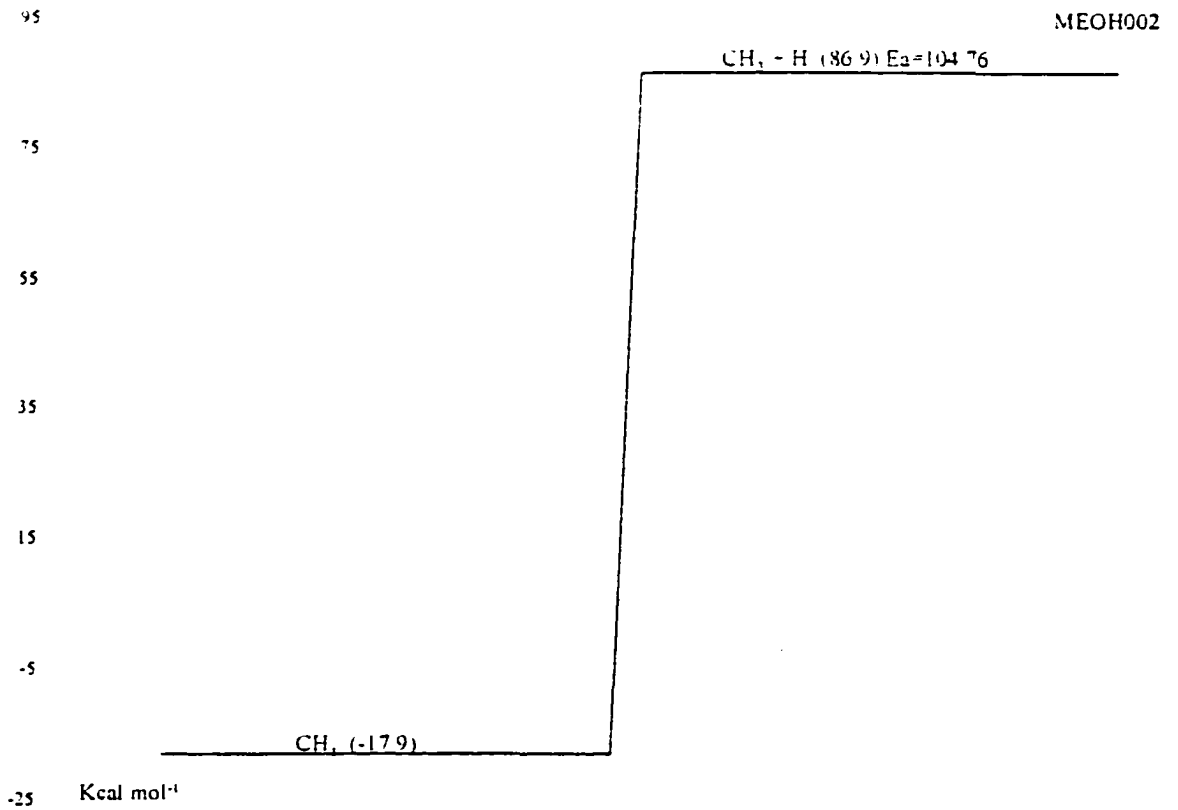


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$CH_2O \rightarrow CHO + H$	3.59×10^{14} T^0 e^{-0T}	88.26
k_2	$CH_2O \rightarrow CO + H_2$	4.52×10^{15} T^0 e^{-0T}	35.30

frequency/degeneracy (CPFIT)
CH_2O: 1071.8 (0.995); 1468.5 (2.766); 2740.8 (2.239)
Lennard-Jones parameter
σ(Å) = 3.59, ε/k (K) = 498.0

k_1 A_f is taken from NIST fit. $E_{a,f} = \Delta U_{rxn} = 88.26$ kcal mol^{-1}.
k_2 NIST fit.

IID. 46 $CH_4 \rightarrow CH_3 + H$

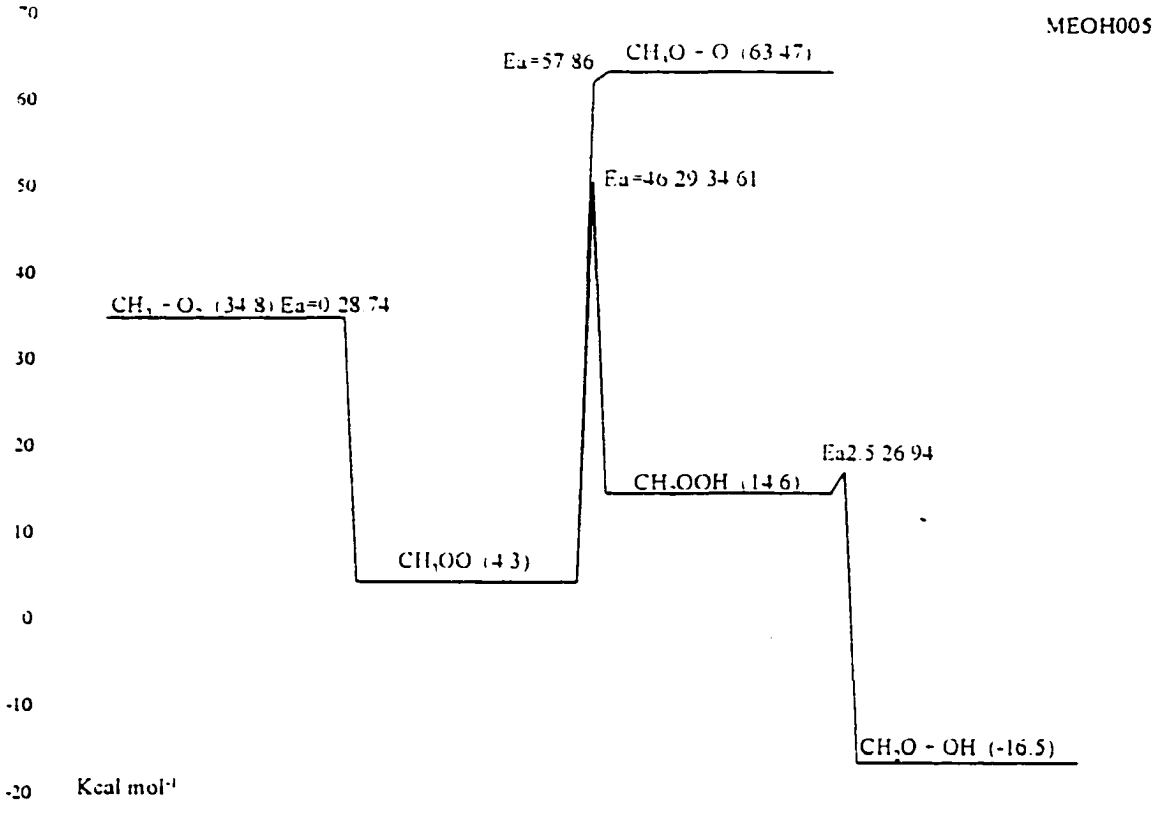


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$CH_4 \rightarrow CH_3 + H$	1.07×10^{16} T^0 e^{-0T}	104.76

frequency/degeneracy (CPFIT)
CH_4: 1106.6 (2.973); 2499.9 (4.410); 3693.3 (1.617)
Lennard-Jones parameter
σ(Å) = 3.75, ε/k (K) = 141.40

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.11 \times 10^{14}$, 92 BAU/COB. $E_{a,f} = E_{a,r}$ (0) + ΔU_{rxn} (104.76) kcal mol^{-1}.

IID. 47 $CH_3 + O_2 \rightarrow$ Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$CH_3 + O_2 \rightarrow CH_3OO.$	1.08×10^{12} T^0 e^{-0T}	0.00
k_{-1}	$CH_3OO. \rightarrow CH_3 + O_2$	2.49×10^{13} T^0 e^{-0T}	28.74
k_2	$CH_3OO. \rightarrow CH_3O + O$	1.36×10^{14} T^0 e^{-0T}	57.86
k_3	$CH_3OO. \rightarrow CH_2OOH$	3.90×10^{10} $T^{1.0}$ e^{-0T}	46.29
k_{-3}	$CH_2OOH \rightarrow CH_3OO.$	3.82×10^{14} $T^{-0.92}$ $e^{-0.00084T}$	34.61
k_4	$CH_2OOH \rightarrow CH_2O + OH$	3.07×10^{12} T^0 e^{-0T}	2.50

frequency/degeneracy (CPFIT)
CH_3OO: 250.3 (2.713); 1091.2 (3.941); 2772.2 (4.846)
Lennard-Jones parameter
σ(Å) = 4.34, ε/k (K) = 422.61

k_1 90 DEM/ASN & 89 ATK/BAU.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -28.74

kcal mol^{-1}.

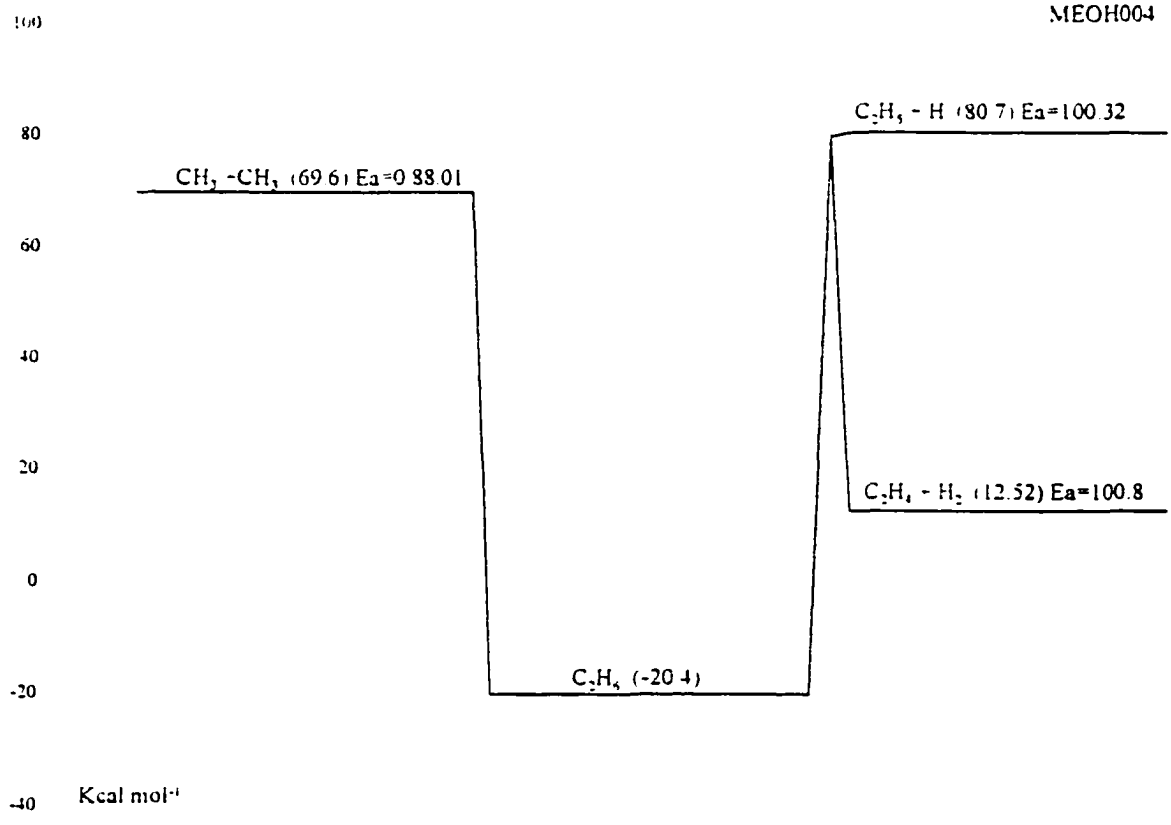
k_2 A_f via A_r and Microscopic Reversbility (MR), A_r =1.51 × 10^{13}, 92 BAU/COB for O + $CH_3O \rightarrow$ Prod.). $E_{a,f} = \Delta U_{rxn}$ = 57.86 kcal mol^{-1}

k_3 A_f estimated using TST, A = (deg.) (ek_b/h) exp($\Delta S^{\ddagger}(T)/R$) T^n, deg. = 3, ek_b/h = 5.66 × 10^{10}, n = 1.0, $\Delta S^{\ddagger}(T)$ is estimated as loss of one rotor (-4.3 kcal mol^{-1}) and gain one optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (8.61) + ΔU_{rxn} (11.68) kcal mol^{-1}

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 11.68 kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), A_r = 2.75 × 10^{12} = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} based on $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O$ + OH (1990 Page)

IID. 48 $CH_3 + CH_3 \rightarrow$ Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$CH_3 + CH_3 \rightarrow C_2H_6$	3.61×10^{13} T^0 e^{-0T}	0.00
k_{-1}	$C_2H_6 \rightarrow CH_3 + CH_3$	4.08×10^{16} T^0 e^{-0T}	88.01
k_2	$C_2H_6 \rightarrow C_2H_5 + H$	1.26×10^{16} T^0 e^{-0T}	100.32
k_3	$C_2H_6 \rightarrow C_2H_4 + H_2$	4.95×10^{20} T^0 e^{-0T}	100.80

frequency/degeneracy (CPFIT)
C_2H_6: 729.3 (4.525); 1333.9 (6.571); 2825.0 (6.404)
Lennard-Jones parameter
σ(Å) = 4.3, ε/k (K) = 252.3

k_1 92 BAU/COB

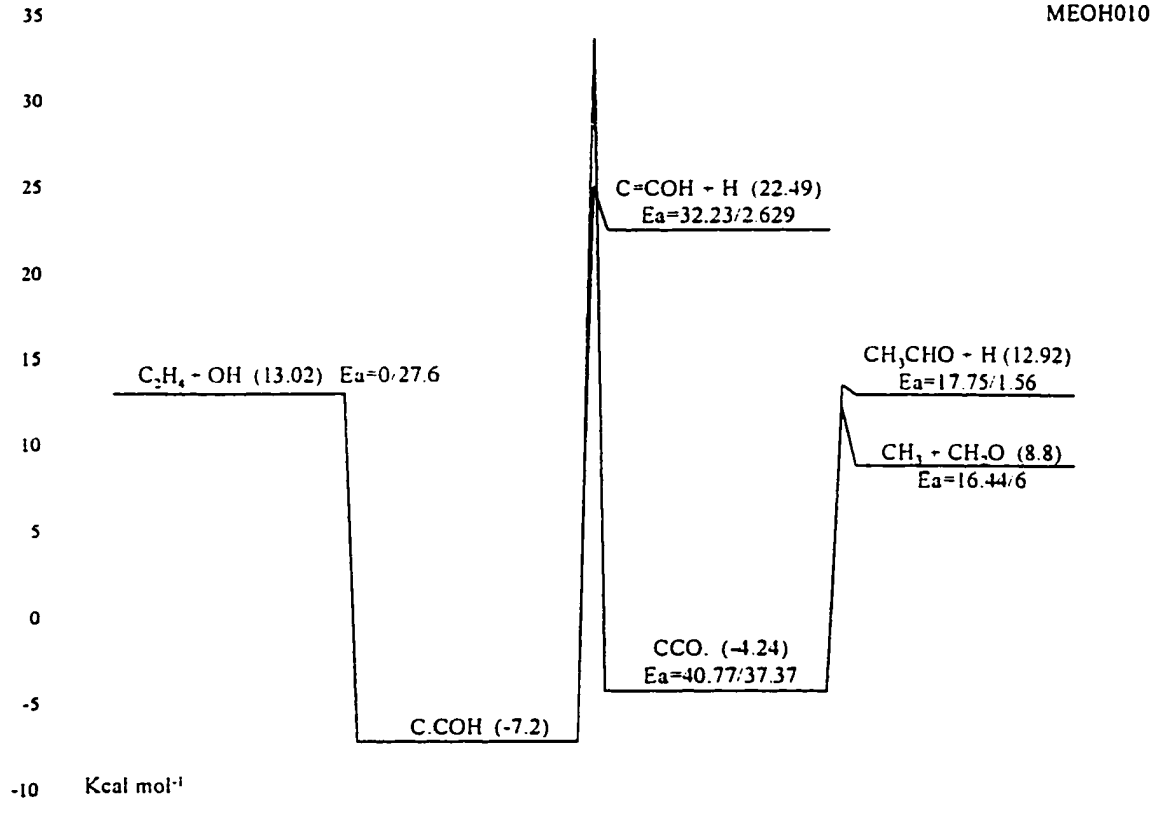
k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 88.01 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{14}$, 93 SIL/RAT. $E_{a,f}$ =

ΔU_{rxn} = 100.32 kcal mol^{-1}.

k_3 A_f is taken from NIST fit. $E_{a,f} = \Delta U_{rxn}$ = 100.80 kcal mol^{-1}.

IID. 49 $C_2H_4 + OH \rightarrow$ Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	$C_2H_4 + OH \rightarrow C.COH$	5.42×10^{12} T^0 e^{-0T}	0.00
k_{-1}	$C.COH \rightarrow C_2H_4 + OH$	7.65×10^{12} T^0 e^{-0T}	27.60
k_2	$C.COH \rightarrow C{=}COH + H$	3.85×10^{11} T^0 e^{-0T}	32.23
k_3	$C.COH \rightarrow CCO.$	8.58×10^{8} $T^{0.97}$ $e^{-0.00042T}$	40.77
k_{-3}	$CCO. \rightarrow C.COH$	1.95×10^{10} $T^{1.0}$ e^{-0T}	37.37
k_4	$CCO. \rightarrow CH_2O + CH_3$	1.04×10^{13} T^0 e^{-0T}	16.44
k_5	$CCO. \rightarrow CH_3CHO + H$	1.73×10^{13} T^0 e^{-0T}	17.75

frequency/degeneracy (CPFIT)
C.COH: 583.0 (5.793); 1512.1 (6.964); 3255.1 (4.243)
CCO.: 619.0 (5.969); 1499.7 (7.377); 3180.0 (4.154)
Lennard-Jones parameter
σ(Å) = 4.35, ε/k (K) = 422.61

k_1 92 BAU/COB.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f}(0) - \Delta U_{rxn}$ (-27.6) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 4.00 \times 10^{12}$, 84 WAR for CC=C + H → CCC.. $E_{a,f} = E_{a,r}$ (2.629) + ΔU_{rxn} (29.6) kcal mol^{-1}.

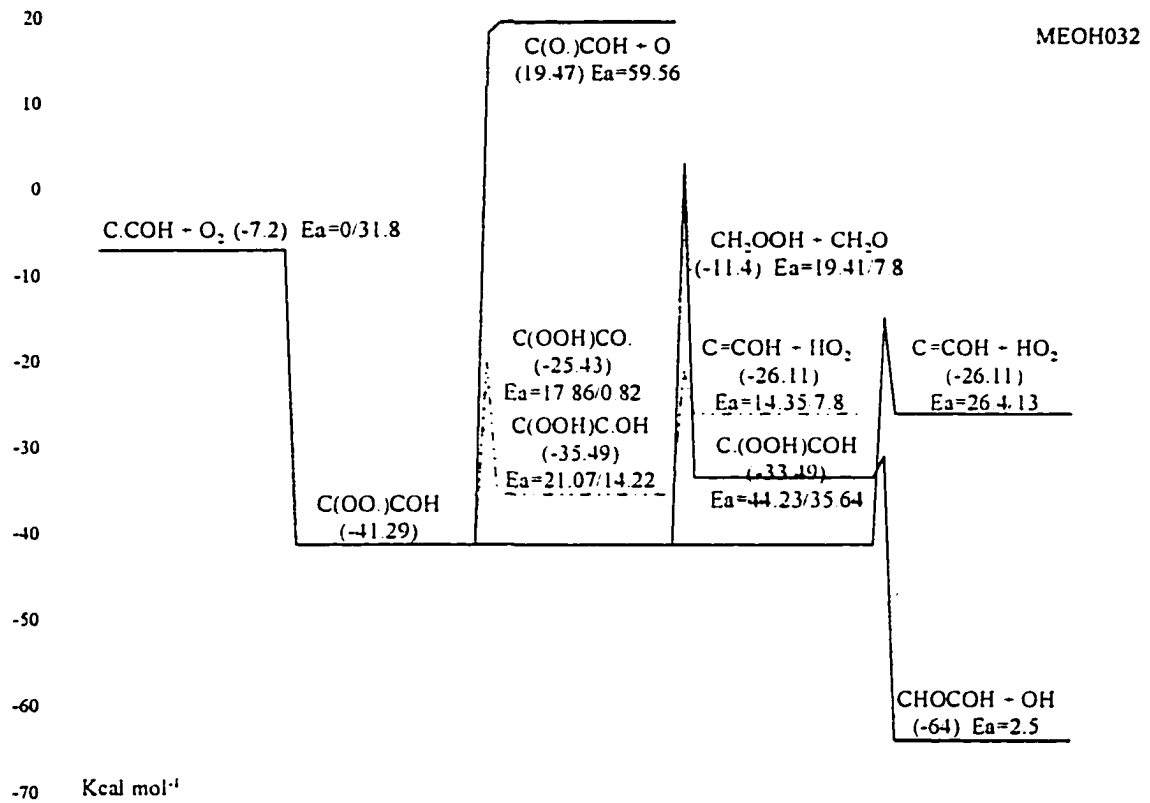
k_{-3} A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (3.4) kcal mol^{-1}.

k_{-3} A_r estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 3, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotors (-4.3 cal mol^{-1} K^{-1}). $E_{a,f}$ = RS (26) + E_{abst} (11.37) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.31 \times 10^{11}$ 86 TSA/HAM for CH_3 + C=C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (10.44) kcal mol^{-1}. $E_{a,r}$ = 6.0 kcal mol^{-1}. (estimated by Bozzelli).

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12}$ = 1/2 (H + CC=C → CC.C, 91 TSA/HAM). $E_{a,f} = E_{a,r}$ (1.56) + ΔU_{rxn} (16.19) kcal mol^{-1}.

IID. 50 C.COH + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C.COH + O_2 → C(OO.)COH	3.01×10^{12} T^0 e^{-0T}	0.00
k_{-1}	C(OO.)COH → C.COH + O_2	5.93×10^{14} T^0 e^{-0T}	31.81
k_2	C(OO.)COH → C(O.)COH + O	2.63×10^{14} T^0 e^{-0T}	59.56
k_3	C(OO.)COH → C=COH + HO_2	1.49×10^{10} $T^{0.74}$ e^{-0T}	26.40
k_4	C(OO.)COH → C.(OOH)COH	2.60×10^{10} $T^{1.0}$ e^{-0T}	44.23
k_{-4}	C.(OOH)COH → C(OO.)COH	6.71×10^{12} $T^{-0.33}$ $e^{-0.00073T}$	35.64
k_5	C.(OOH)COH → CHOCOH + OH	1.16×10^{13} T^0 e^{-0T}	2.50
k_6	C(OO.)COH → C(OOH)C.OH	2.99×10^{9} $T^{1.0}$ e^{-0T}	21.07
k_{-6}	C(OOH)C.OH → C(OO.)COH	2.52×10^{13} $T^{-0.68}$ $e^{-0.00087T}$	14.22
k_7	C(OOH)C.OH → C=COH + HO_2	2.41×10^{12} T^0 e^{-0T}	14.35
k_8	C(OO.)COH → C(OOH)CO.	1.72×10^{8} $T^{1.0}$ e^{-0T}	17.86
k_{-8}	C(OOH)CO. → C(OO.)COH	1.72×10^{11} $T^{-0.06}$ $e^{-0.00009T}$	0.82
k_9	C(OOH)CO. → CH_2O + CH_2OOH	6.82×10^{13} T^0 e^{-0T}	19.41

frequency/degeneracy (CPFIT)
C(OO.)COH: 265.0 (6.738); 1167.8 (9.006); 2891.9 (6.756)
C.(OOH)COH: 257.1 (8.192); 1237.6 (8.815); 2903.7 (4.993)
C(OOH)C.OH: 299.8 (8.560); 1190.9 (8.506); 2901.2 (4.933)
C(OOH)CO.: 277.1 (7.323); 1180.9 (10.312); 2843.6 (4.865)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 89 ATK/BAU and 90 DEM/SAN for CC. + O_2.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-31.81) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for O + $CH_3O \rightarrow$ Prod.. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (59.56) kcal mol^{-1}.

k_3 A_f is referenced from reaction C2CCOO. $\rightarrow$ C2C=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (13.40) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_4 A_f estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}(T)/R$), deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (9.64) + ΔH_{rxn} (8.59) kcal mol^{-1}.

k_{-4} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (8.59) kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O$ + OH (1990 Page)

k_6 A_f estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}(T)/R$), deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (8.22) + ΔH_{rxn} (6.85) kcal mol^{-1}.

k_{-6} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (6.85) kcal mol^{-1}.

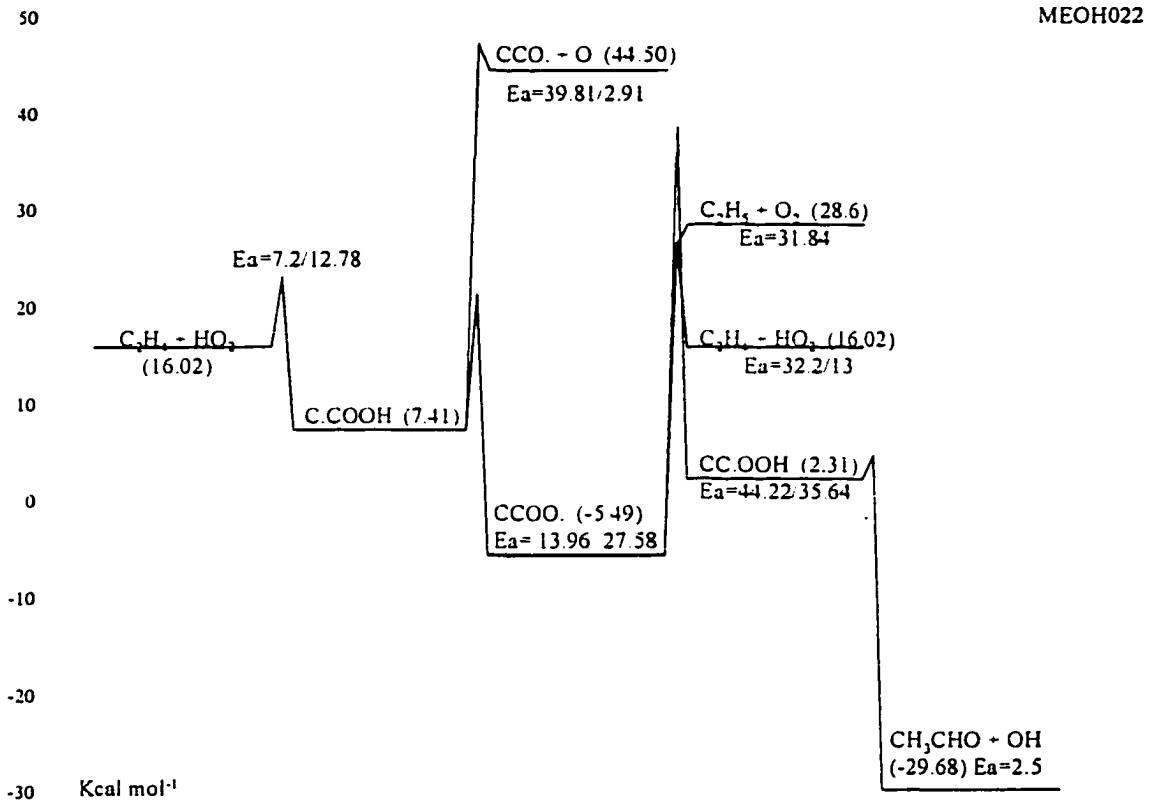
k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.50 \times 10^{11}$ = 1/2 (HO_2 + C=C), 72 KER/PAR. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (6.55) kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_8 A_f estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}(T)/R$), deg. = 3, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (0) + E_{abst} (6.82) - H bond (6) + ΔH_{rxn} (17.04) kcal mol^{-1}.

k_{-8} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (17.04) kcal mol^{-1}.

k_9 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.31 \times 10^{11}$, 86 TSA/HAM and 72 KER/PAR for C=C + CH_3. $E_{a,f} = E_{a,r}$ (7.8) + ΔU_{rxn} (11.61) kcal mol^{-1}.

IID. 51 $C_2H_4 + HO_2 \rightarrow$ Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$C_2H_4 + HO_2 \rightarrow C.COOH$	3.50×10^{11} T^0 e^{-0T}	7.20
k_{-1}	$C.COOH \rightarrow C_2H_4 + HO_2$	8.23×10^{11} T^0 e^{-0T}	12.78
k_2	$C.COOH \rightarrow C{=}COOH + H$	7.61×10^{11} T^0 e^{-0T}	39.81
k_3	$C.COOH \rightarrow CCOO.$	2.14×10^{11} $T^{-0.12}$ $e^{-0.00057T}$	13.96
k_{-3}	$CCOO. \rightarrow C.COOH$	4.49×10^{9} $T^{1.0}$ e^{-0T}	27.58
k_4	$CCOO. \rightarrow C_2H_5 + O_2$	2.99×10^{14} T^0 e^{-0T}	31.84
k_5	$CCOO. \rightarrow C_2H_4 + HO_2$	2.24×10^{10} $T^{0.74}$ e^{-0T}	32.20
k_6	$CCOO. \rightarrow CC.OOH$	2.60×10^{10} $T^{1.0}$ e^{-0T}	44.22
k_{-6}	$CC.OOH \rightarrow CCOO.$	6.77×10^{12} $T^{-0.33}$ $e^{-0.00075T}$	35.64
k_7	$CC.OOH \rightarrow CH_3CHO + OH$	1.15×10^{13} T^0 e^{-0T}	2.50

frequency/degeneracy (CPFIT)
CCOO.: 250.3 (4.749); 1127.3 (8.486); 2761.8 (6.765)
C.COOH: 251.0 (5.710); 1184.3 (9.067); 2804.0 (4.723)
CC.OOH: 100.4 (5.313); 1071.3 (8.260); 2583.3 (5.926)

Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 estimated by Bozzelli.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-5.58) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 7.23 \times 10^{12}$, 91 TSA/HAM for H + CC=C → CCC.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (36.9) kcal mol^{-1}. $E_{a,r}$ = 2.906 kcal mol^{-1}. (taken from the same reference).

k_3 A_f estimated using TST, A = (deg.) (ek_b/h) $\exp(\Delta S^{\neq}(T)/R)$ T^n, deg. = 3, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 kcal mol^{-1}) and gain one optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (7.96) + ΔH_{rxn} (13.62) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (13.62) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.01 \times 10^{12}$, 90 DEM/ASN and 89 ATK/BAU. $E_{a,f} = E_{a,r}$ (0) + ΔU_{rxn} (31.84) kcal mol^{-1}.

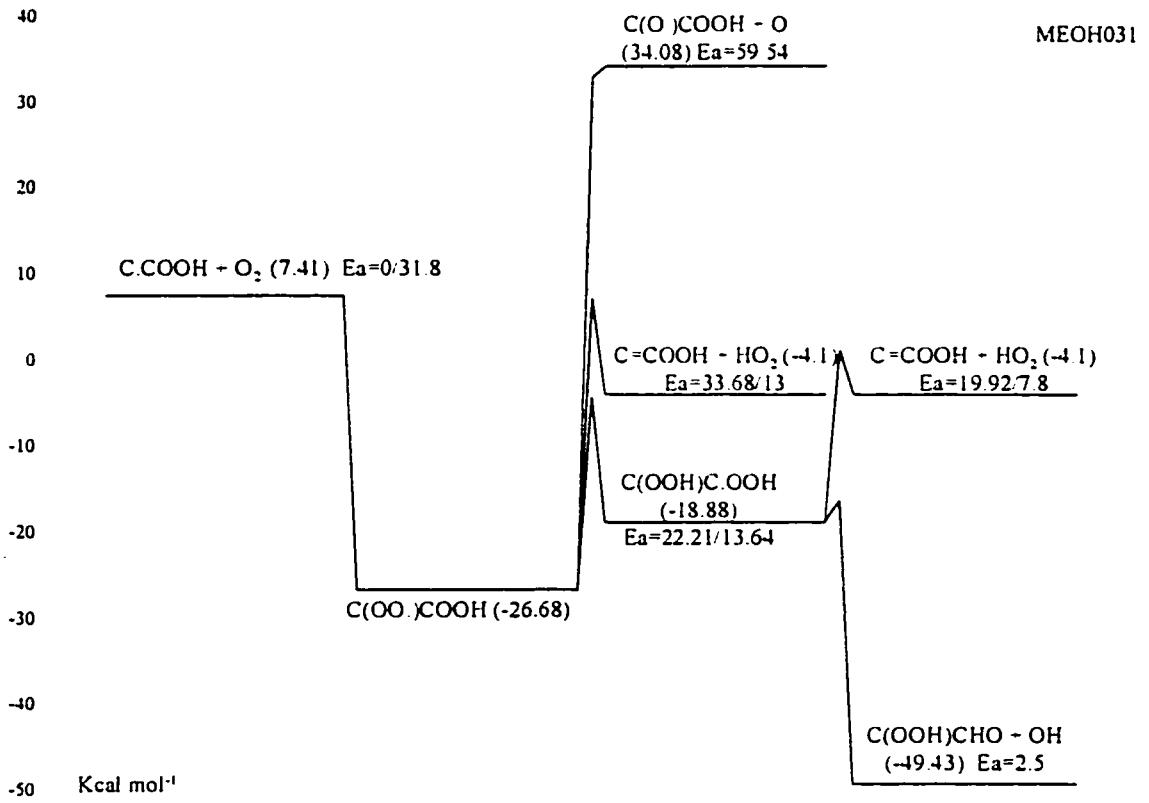
k_5 A_f is referenced from reaction C2CCOO. → C2C=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (19.20) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_6 A_f estimated using TST, A = (deg.) (ek_b/h) $\exp(\Delta S^{\neq}(T)/R)$ T^n, deg. = 2, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 kcal mol^{-1}) and gain one optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (9.64) + ΔH_{rxn} (8.58) kcal mol^{-1}.

k_{-6} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (8.58) kcal mol^{-1}.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} based on $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

IID. 52 C.COOH + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C.COOH + O_2 → C(OO.)COOH	3.01×10^{12} T^0 e^{-0T}	0.00
k_{-1}	C(OO.)COOH → C.COOH + O_2	6.34×10^{14} T^0 e^{-0T}	31.80
k_2	C(OO.)COOH → C(O.)COOH + O	2.61×10^{14} T^0 e^{-0T}	59.54
k_3	C(OO.)COOH → C=COOH + HO_2	1.49×10^{10} $T^{0.74}$ e^{-0T}	33.68
k_4	C(OO.)COOH → C(OOH)C.OOH	2.99×10^{9} $T^{1.0}$ e^{-0T}	22.21
k_{-4}	C(OOH)C.OOH → C(OO.)COOH	8.68×10^{11} $T^{-0.36}$ $e^{-0.00078T}$	13.64
k_5	C(OOH)C.OOH → C=COOH + HO_2	7.40×10^{11} T^0 e^{-0T}	19.92
k_6	C(OOH)C.OOH → C(OOH)CHO + OH	1.88×10^{13} T^0 e^{-0T}	2.50

frequency/degeneracy (CPFIT)
C(OO.)COOH: 100.4 (7.902); 1049.4 (10.517); 2637.2 (6.581)
C(OOH)C.OOH: 100.1 (9.454); 1121.1 (10.325); 2623.9 (4.720)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 89 ATK/BAU and 90 DEM/SAN for CC. + O_2.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-31.80) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for $O + CH_3O \rightarrow$ Prod.. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (59.54) kcal mol^{-1}.

k_3 A_f is referenced from reaction C2CCOO. $\rightarrow$ C2C=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,f}$ (13) + ΔU_{rxn} (20.68) kcal mol^{-1}.$E_{a,R}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

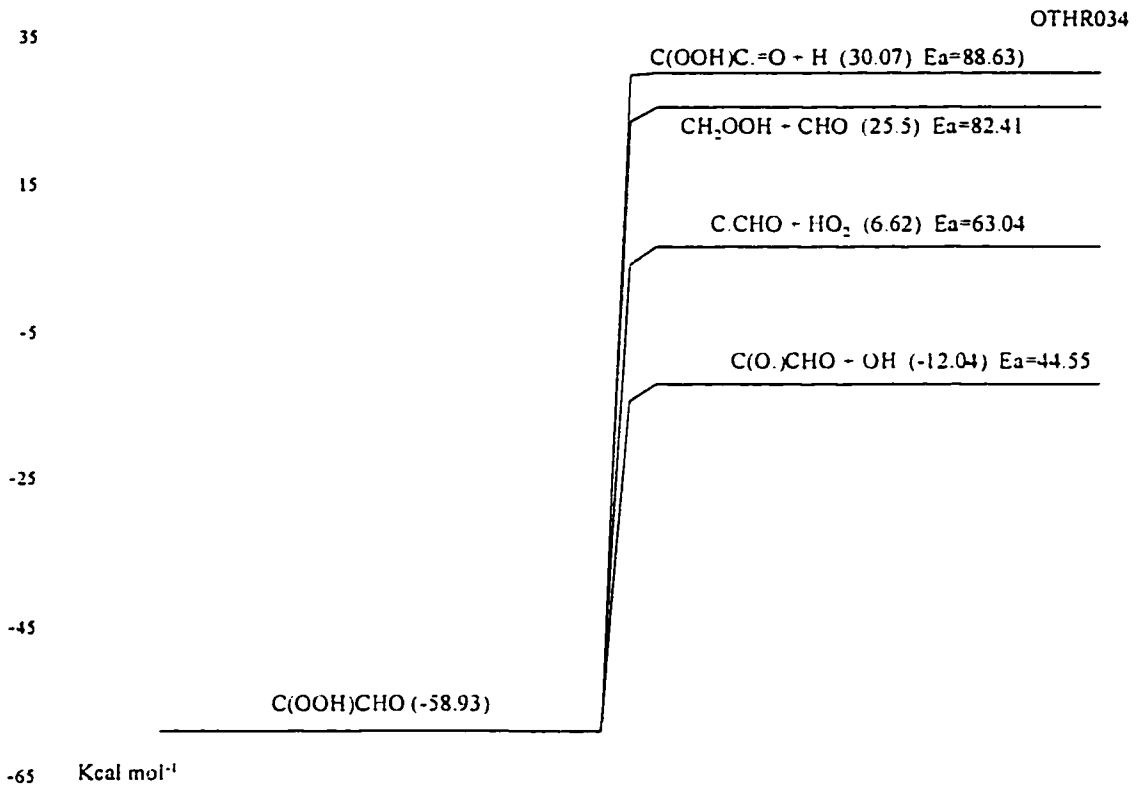
k_4 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 $\times$ 2 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (7.64) + ΔH_{rxn} (8.57) kcal mol^{-1}.

k_{-4} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-8.57) kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.50 \times 10^{11}$ = 1/2 (HO_2 + C=C), 72 KER/PAR. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (12.12) kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O$ + OH (1990 Page)

IID. 53 C(OOH)CHO → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C(OOH)CHO → C(OOH)C.=O + H	1.36×10^{15} T^0 e^{-0T}	88.63
k_2	C(OOH)CHO → CHO + CH_2OOH	3.48×10^{16} T^0 e^{-0T}	82.41
k_3	C(OOH)CHO → C.CHO + HO_2	4.30×10^{14} T^0 e^{-0T}	63.04
k_3	C(OOH)CHO → C(O.)CHO + OH	1.49×10^{15} T^0 e^{-0T}	44.55

frequency/degeneracy (CPFIT)
C(OOH)CHO: 317.6 (6.233); 800.4 (4.689); 2043.0 (8.578)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

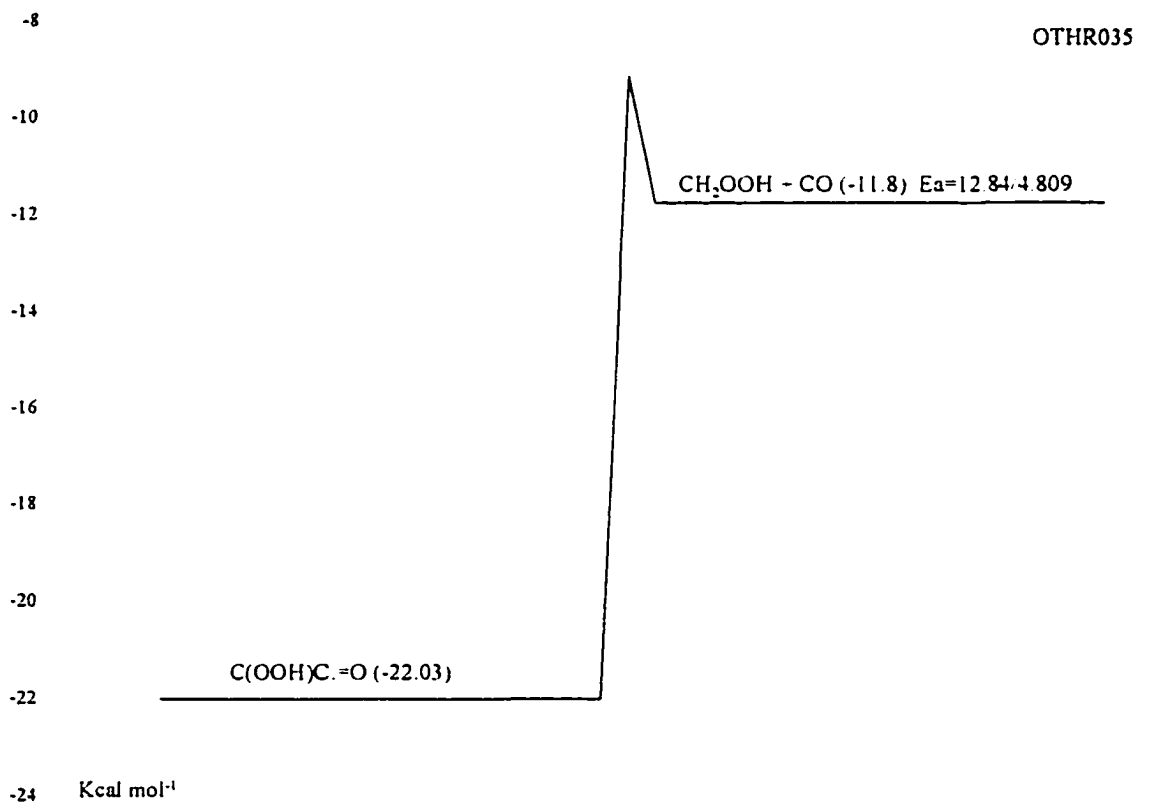
k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{13}$ = 1/2 (H + CHO), NIST FIT. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (88.63) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, 86 TSA/HAM for CH_3 + CHO. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (82.41) kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{12}$, 91 TSA/HAM for C=CC. + $HO_2 \rightarrow$ C=CCO. + OH. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (63.04) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, 86 TSA/HAM for $CH_3O + OH \rightarrow H_2O + CH_2O$. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (44.55) kcal mol^{-1}.

IID. 54 $C(OOH)C.=O \rightarrow CH_2OOH + CO$

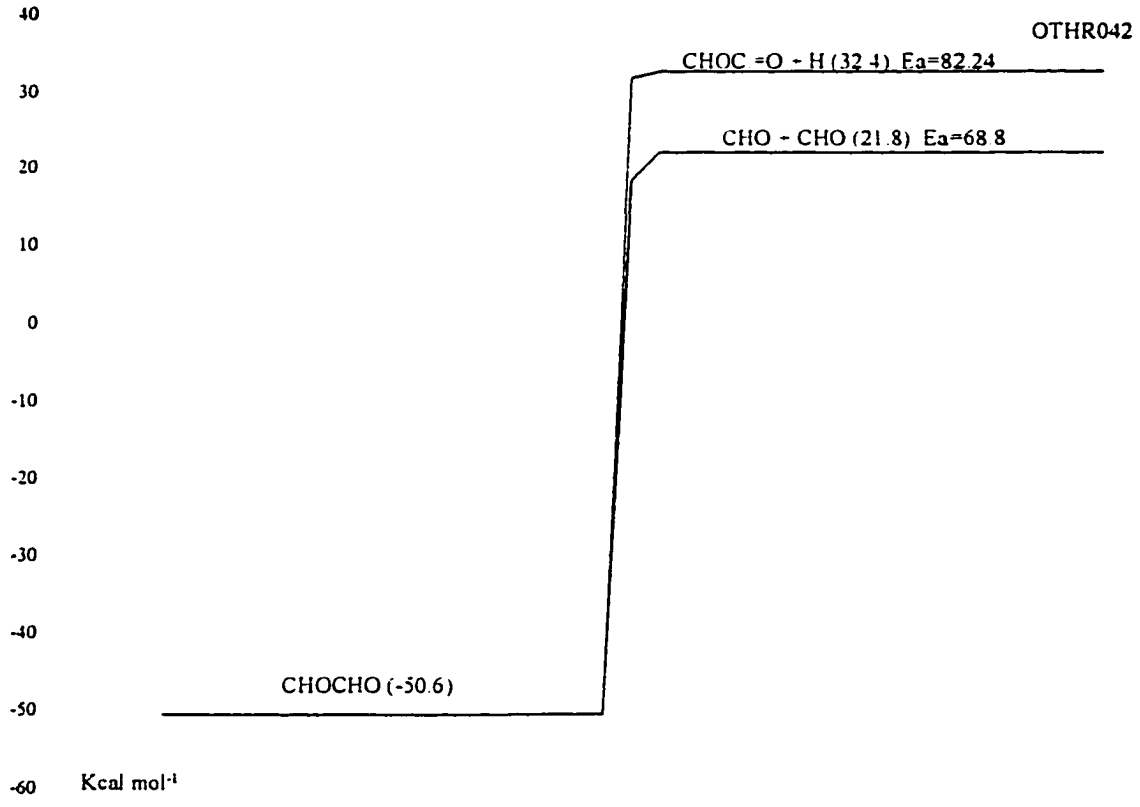


	Reaction	A $T^n e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	$C(OOH)C.=O \rightarrow CH_2OOH + CO$	6.10×10^{12} T^0 e^{-0T}	12.84

frequency/degeneracy (CPFIT)
C(OOH)C.=O: 413.5 (6.396); 407.2 (2.854); 1856.0 (7.249)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{11}$, 86 TSA/HAM for CC. + CO. $E_{a,f} = E_{a,f}$ (4.809) + ΔU_{rxn} (8.03) kcal mol^{-1}.

IID. 55 CHOCHO → Products



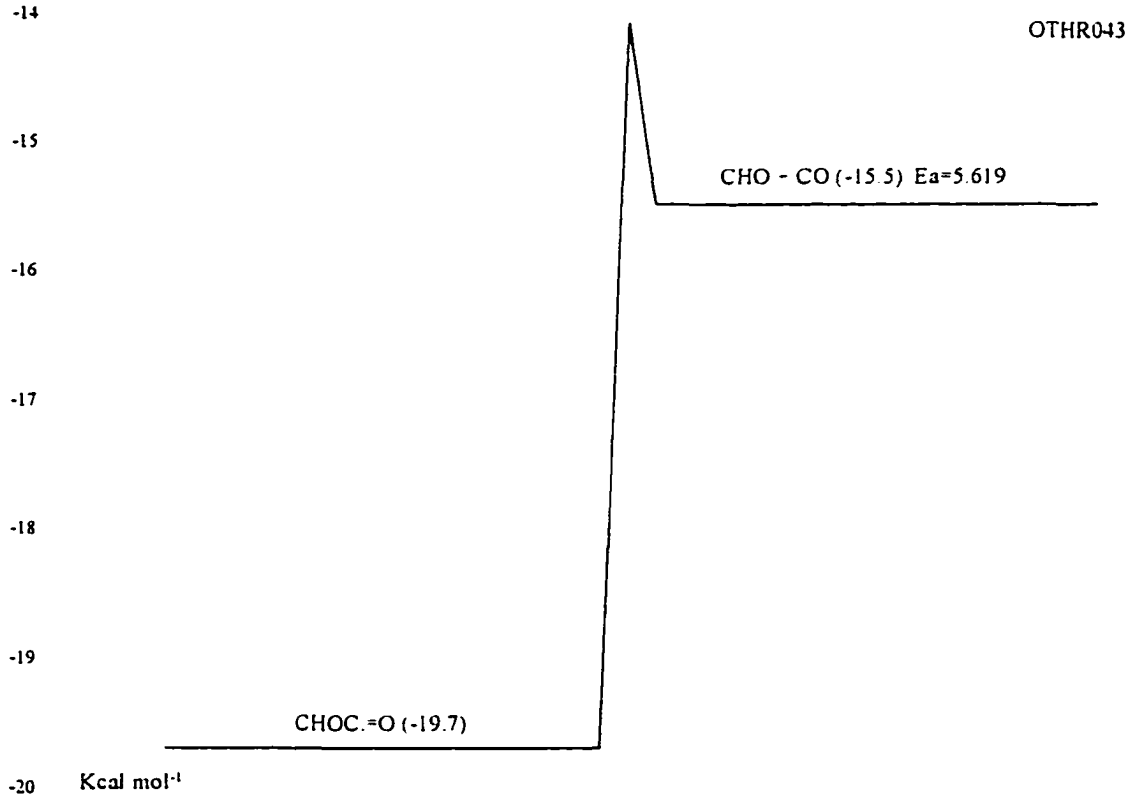
	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CHOCHO → CHOC.=O + H	5.94×10^{14} T^0 e^{-0T}	82.24
k_2	CHOCHO → CHO + CHO	5.66×10^{16} T^0 e^{-0T}	68.80

frequency/degeneracy (CPFIT)
CHOCHO: 516.1 (5.362); 1504.9 (5.604); 3990.9 (0.534)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{13}$ = 1/2 (H + CHO), NIST FIT. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (82.24) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.01 \times 10^{11}$, 85 STO/SCH. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (68.8) kcal mol^{-1}.

IID. 56 CHOC.=O → CHO + CO

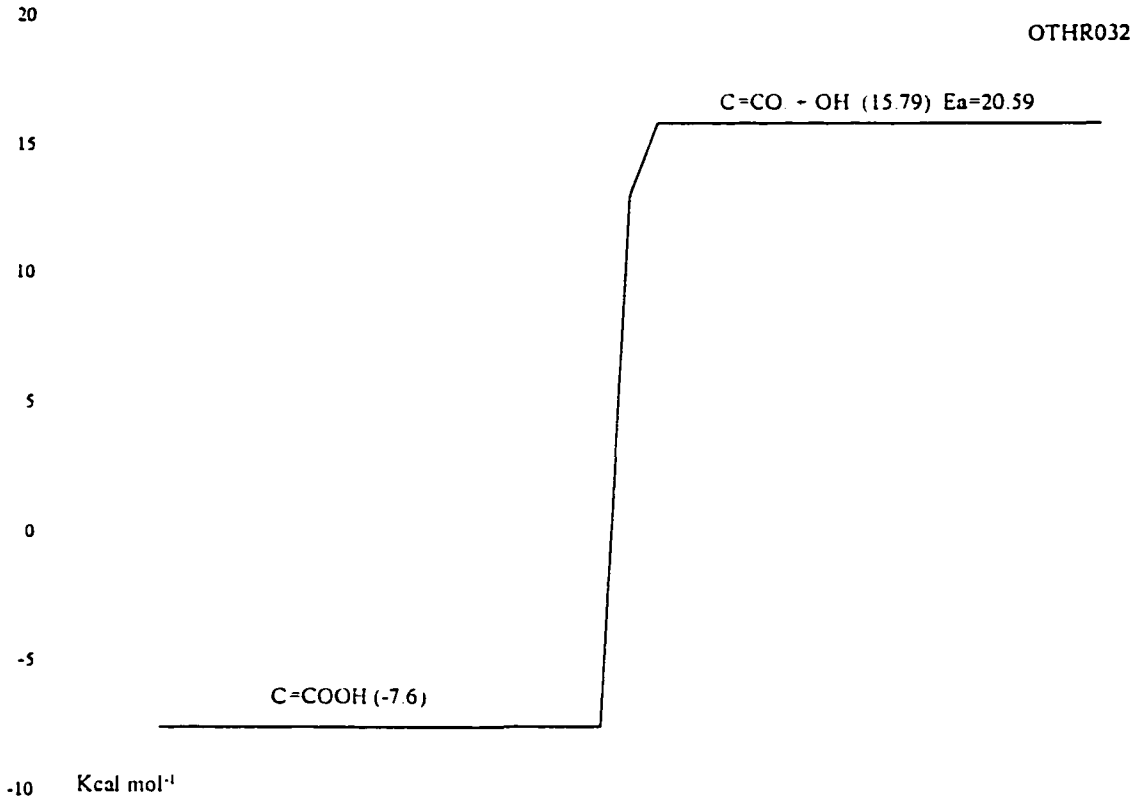


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CHOC.=O → CHO + CO	1.37×10^{13} T^0 e^{-0T}	5.62

frequency/degeneracy (CPFIT)
CHOC.=O: 435.1 (3.791); 800.3 (2.166); 1849.1 (2.544)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{11}$, 86 TSA/HAM for CO + C=C.. $E_{a,f} = E_{a,r}$ (4.809) + ΔU_{rxn} (0.81) kcal mol^{-1}.

IID. 57 C=COOH → C=CO. + OH

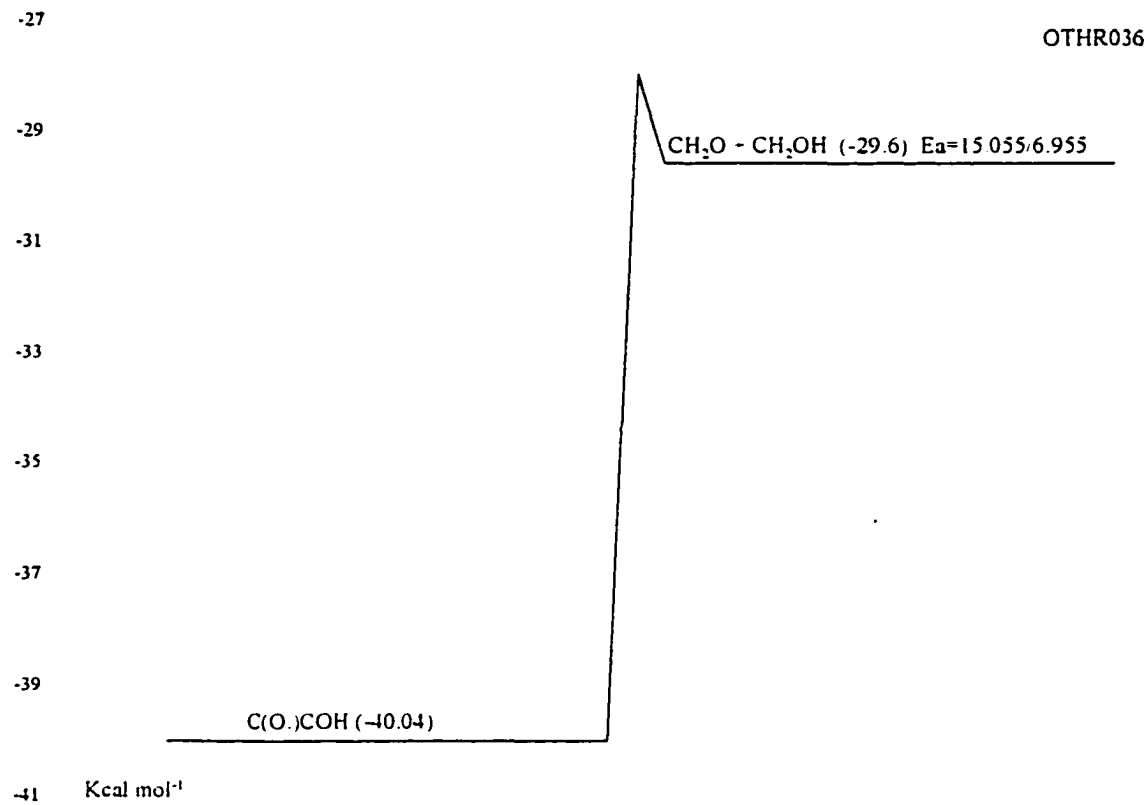


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C=COOH → C=CO. + OH	1.58×10^{15} T^0 e^{-0T}	20.59

frequency/degeneracy (CPFIT)
C=COOH: 385.4 (5.761); 1193.2 (8.293); 2866.8 (2.946)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 91 TSA/HAM for C=CC. + OH. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (20.59) kcal mol^{-1}.

IID. 58 $C(O.)COH \rightarrow CH_2O + CH_2OH$

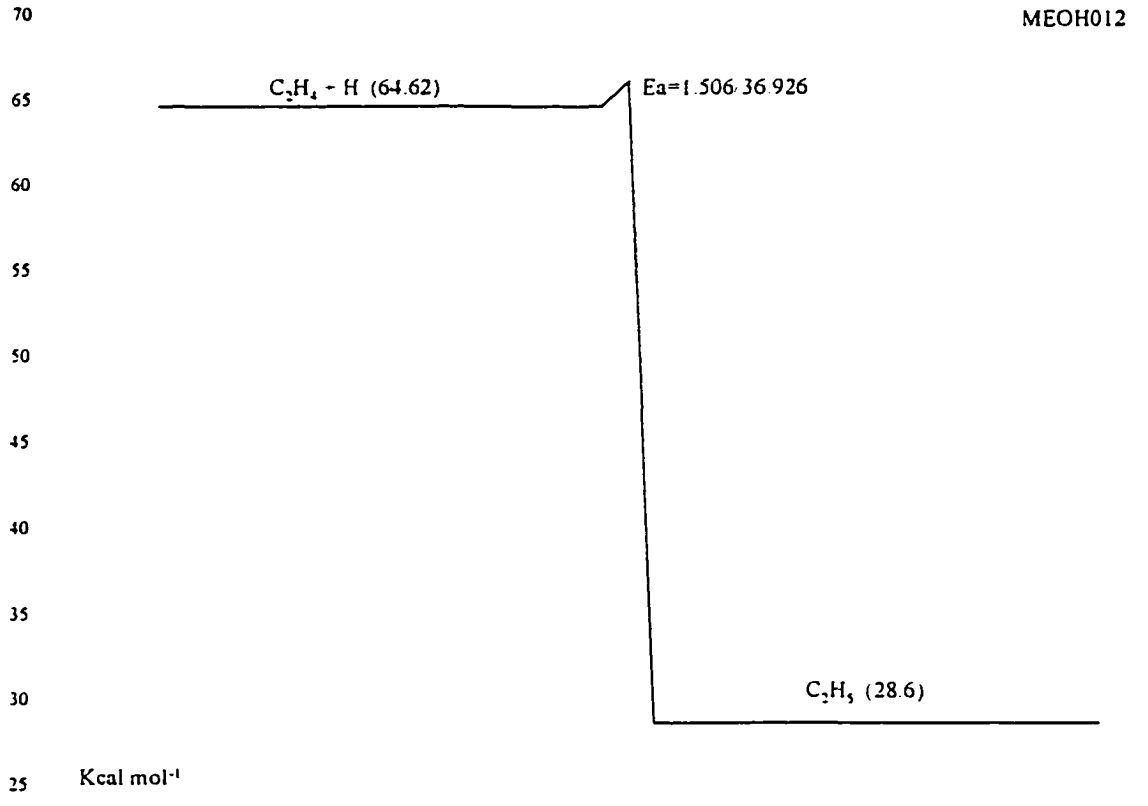


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	$C(O.)COH \rightarrow CH_2O + CH_2OH$	4.84×10^{12} T^0 e^{-0T}	15.06

frequency/degeneracy (CPFIT)
C(O.)COH: 509.7 (7.126); 1415.0 (8.212); 3225.7 (4.662)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 4.82 \times 10^{10}$, 86 TSA/HAM for C=C + CH_2OH. $E_{a,f} = E_{a,f}$ (6.955) + ΔU_{rxn} (8.10) kcal mol^{-1}.

IID. 59 $C_2H_5 \rightarrow C_2H_4 + H$

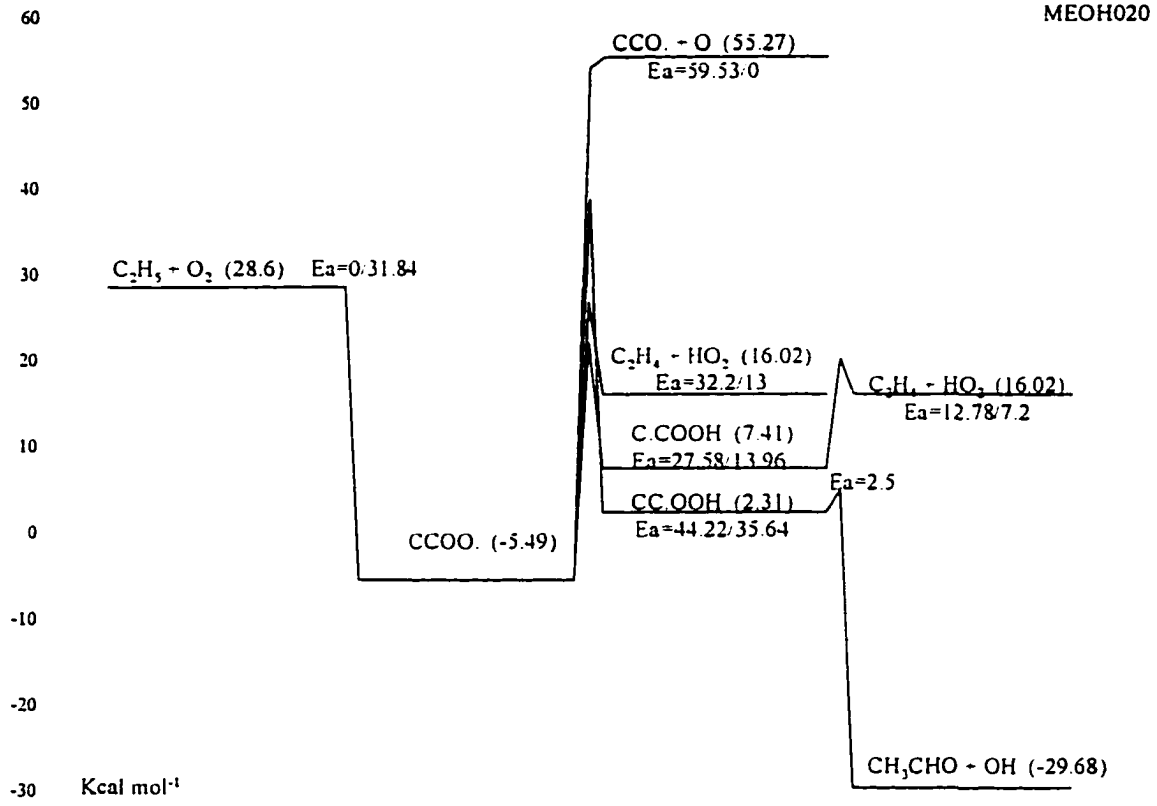


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	$C_2H_5 \rightarrow C_2H_4 + H$	2.92×10^{12} T^0 e^{-0T}	36.93

frequency/degeneracy (CPFIT)
C_2H_5: 728.5 (3.698); 1311.6 (5.239); 2771.8 (5.563)
Lennard-Jones parameter
σ(Å) = 4.30, ε/k (K) = 252.30

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{13}$, 84 WAR. $E_{a,f} = E_{a,r}$ (1.506) + ΔU_{rxn} (36.93) kcal mol^{-1}.

IID. 60 $C_2H_5 + O_2 \rightarrow$ Products



	Reaction	A $T^n e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$C_2H_5 + O_2 \rightarrow CCOO.$	$3.01\times10^{12}\ T^0\ e^{-0T}$	0.00
k_{-1}	$CCOO. \rightarrow C_2H_5 + O_2$	$2.99\times10^{14}\ T^0\ e^{-0T}$	31.84
k_2	$CCOO. \rightarrow CCO. + O$	$2.59\times10^{14}\ T^0\ e^{-0T}$	59.53
k_3	$CCOO. \rightarrow C_2H_4 + HO_2$	$2.24\times10^{10}\ T^{0.74}\ e^{-0T}$	32.20
k_4	$CCOO. \rightarrow C.COOH$	$4.49\times10^{9}\ T^{1.0}\ e^{-0T}$	27.58
k_{-4}	$C.COOH \rightarrow CCOO.$	$2.14\times10^{11}\ T^{-0.12}\ e^{-0.00057T}$	13.96
k_5	$C.COOH \rightarrow C_2H_4 + HO_2$	$8.23\times10^{11}\ T^0\ e^{-0T}$	12.78
k_6	$CCOO. \rightarrow CC.OOH$	$2.60\times10^{10}\ T^{1.0}\ e^{-0T}$	44.22
k_{-6}	$CC.OOH \rightarrow CCOO.$	$6.77\times10^{12}\ T^{-0.33}\ e^{-0.00075T}$	35.64
k_7	$CC.OOH \rightarrow CH_3CHO + OH$	$1.15\times10^{13}\ T^0\ e^{-0T}$	2.50

frequency/degeneracy (CPFIT)
CCOO.: 250.3 (4.749); 1127.3 (8.486); 2761.8 (6.765)
C.COOH: 251.0 (5.710); 1184.3 (9.067); 2804.0 (4.723)
CC.OOH: 100.4 (5.313); 1071.3 (8.260); 2583.3 (5.926)

Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 90 DEM/ASN and 89 ATK/BAU

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f}(0) - \Delta U_{rxn}$ (-31.84) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for $O + CH_3O \rightarrow$ Prod.. $E_{a,f} = E_{a,r}(0) + \Delta U_{rxn}$ (59.53) kcal mol^{-1}.

k_3 A_f is referenced from reaction C2CCOO. $\rightarrow$ C2C=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (19.20) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_4 A_f estimated using TST, A = (deg.) (ek_b/h) $\exp(\Delta S^{\neq}(T)/R)$ T^n, deg. = 3, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 kcal mol^{-1}) and gain one optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (7.96) + ΔH_{rxn} (13.62) kcal mol^{-1}.

k_{-4} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (13.62) kcal mol^{-1}.

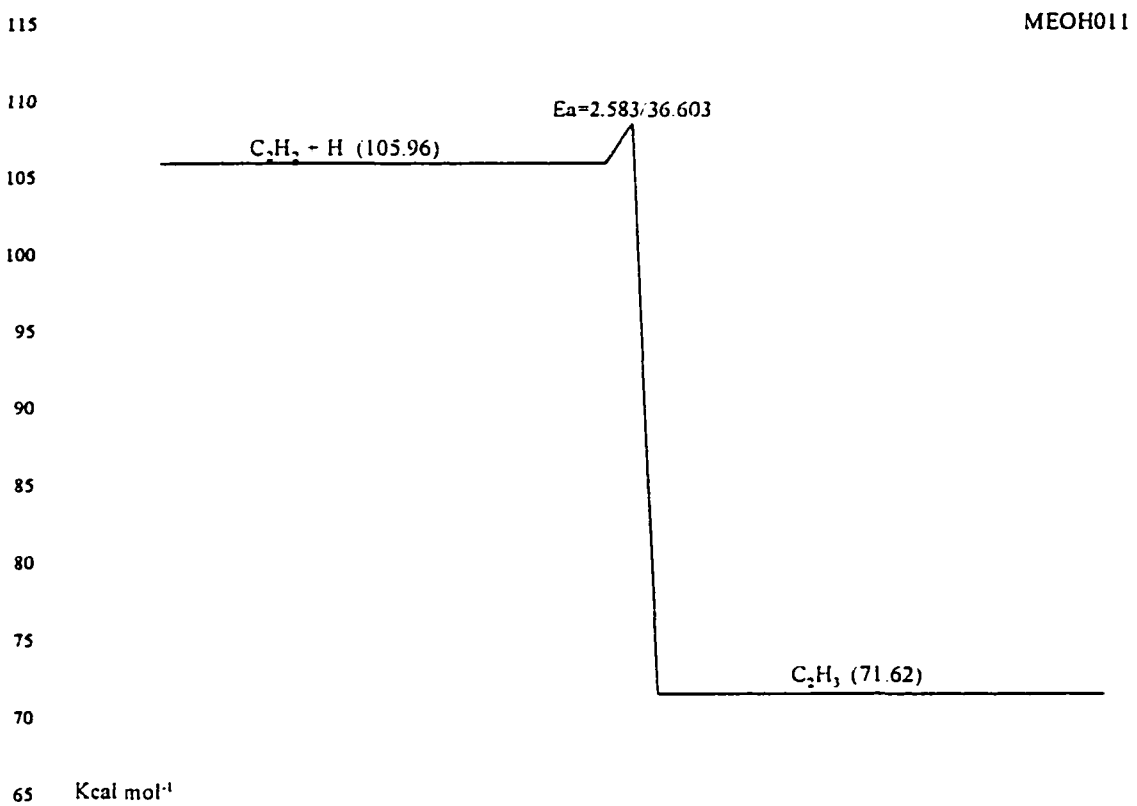
k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.50 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r}$ + ΔU_{rxn} (5.58) kcal mol^{-1}. $E_{a,r}$ = 7.2 kcal mol^{-1}. (estimated by Bozzelli).

k_6 A_f estimated using TST, A = (deg.) (ek_b/h) $\exp(\Delta S^{\neq}(T)/R)$ T^n, deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 kcal mol^{-1}) and gain one optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (9.64) + ΔH_{rxn} (8.58) kcal mol^{-1}.

k_{-6} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (8.58) kcal mol^{-1}.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} based on $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O$ + OH (1990 Page)

IID. 61 $C_2H_3 \rightarrow C_2H_2 + H$

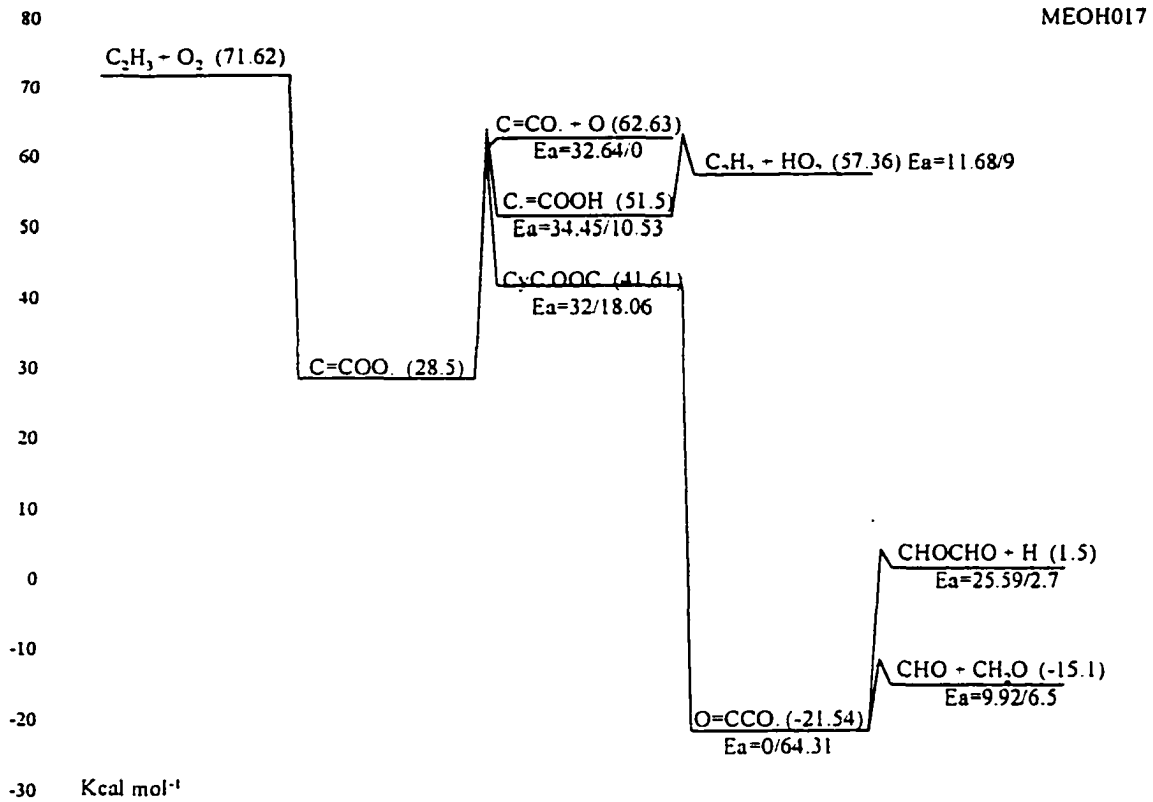


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	$C_2H_3 \rightarrow C_2H_2 + H$	3.60×10^{12} T^0 e^{-0T}	36.60

frequency/degeneracy (CPFIT)
C_2H_3: 871.1 (2.528); 1155.4 (2.961); 2876.1 (3.511)
Lennard-Jones parameter
σ(Å) = 4.10, ε/k (K) = 209.00

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 8.43 \times 10^{12}$, 92 BAU/COB. $E_{a,f} = E_{a,r}$ (2.583) + ΔU_{rxn} (34.02) kcal mol^{-1}.

IID. 62 $C_2H_3 + O_2 \rightarrow$ Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1})	E_a (kcal mol^{-1})
k_1	$C_2H_3 + O_2 \rightarrow C{=}COO.$	4.00×10^{12} T^0 e^{-0T}	0.00
k_{-1}	$C{=}COO. \rightarrow C_2H_3 + O_2$	4.31×10^{14} T^0 e^{-0T}	40.65
k_2	$C{=}COO. \rightarrow C{=}CO. + O$	2.00×10^{14} T^0 e^{-0T}	32.64
k_3	$C{=}COO. \rightarrow C.{=}COOH$	2.60×10^{10} $T^{1.0}$ e^{-0T}	34.45
k_{-3}	$C.{=}COOH \rightarrow C{=}COO.$	2.20×10^{13} $T^{-0.44}$ $e^{-0.00073T}$	10.53
k_4	$C.{=}COOH \rightarrow C_2H_2 + HO_2$	1.13×10^{12} T^0 e^{-0T}	11.68
k_5	$C{=}COO. \rightarrow CyC.OOC$	4.08×10^{12} T^0 e^{-0T}	32.00
k_{-5}	$CyC.OOC \rightarrow C{=}COO.$	3.16×10^{13} T^0 e^{-0T}	18.06
k_6	$CyC.OOC \rightarrow O{=}CCO.$	7.45×10^{13} T^0 e^{-0T}	1.00
k_{-6}	$O{=}CCO. \rightarrow CyC.OOC$	4.08×10^{12} T^0 e^{-0T}	65.31
k_7	$O{=}CCO. \rightarrow CH_2O + CHO$	2.35×10^{12} T^0 e^{-0T}	8.87
k_8	$O{=}CCO. \rightarrow CHOCHO + H$	2.77×10^{12} T^0 e^{-0T}	25.59

frequency/degeneracy (CPFIT)
C=COO.: 402.7 (4.812); 1181.7 (5.956); 2794.2 (3.732)

C.=COOH: 328.5 (5.086); 1086.0 (6.740); 2682.1 (2.173)
CyC.OOC: 250.3 (0.359); 904.8 (10.622); 2067.8 (4.019)
O=CCO.: 458.0 (6.266); 1848.3 (7.107); 3996.1 (1.126)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 90 DEM/ASN for $C_2H_3 + O_2 \rightarrow$ Prod.

k_{-1} A_r via $_{Af}$ and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f}(0) - \Delta U_{rxn}$ (-40.65) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for $O + CH_3O \rightarrow$ Prod.. $E_{a,f} = E_{a,r}(0) + \Delta U_{rxn}$ (32.64) kcal mol^{-1}.

k_3 A_f estimated using TST, $A = (deg.)(ek_b/h)\exp(\Delta S^{\neq}(T)/R)\,T^n$, deg. = 2, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 kcal mol^{-1}) and gain one optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (4.53) + ΔH_{rxn} (23.92) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (23.92) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.21 \times 10^{11}$, 86 TSA for $C_2H_2 + CH_3O \rightarrow$ Prod.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (2.68) kcal mol^{-1}. $E_{a,r}$ = 9.0 kcal mol^{-1}. (estimated by Bozzelli).

k_5 A_f estimated using TST, $A = (deg.)(ek_bT/h)\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$?, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f}$ is estimated as ring strain (26) + $E_{a,add}$ (6).

k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (13.94) kcal mol^{-1}.

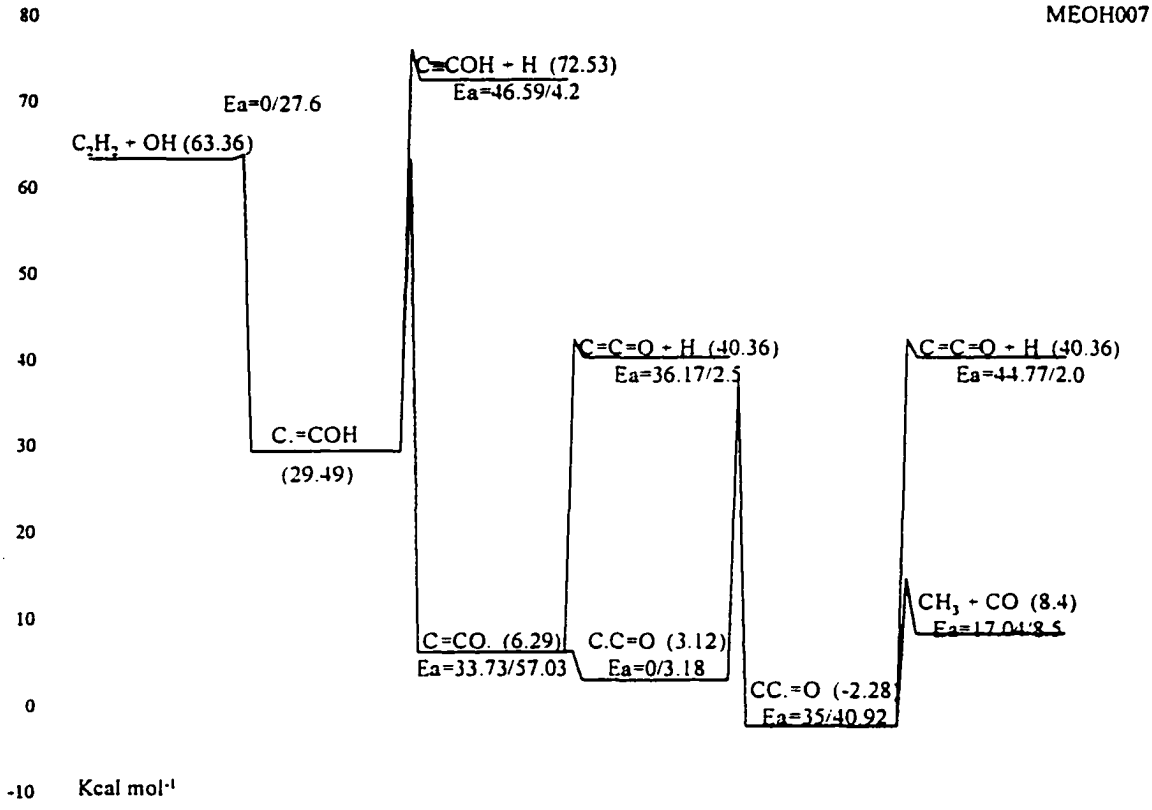
k_6 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f}$ is estimated as 1.0 kcal mol^{-1} by Bozzelli.

k_{-6} A_r estimated using TST, $A = (deg.)(ek_bT/h)\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$?, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-64.31) kcal mol^{-1}.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.04 \times 10^{10}$, 86 LES/ROU for $CHO + C{=}C \rightarrow$ Prod.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (3.42) kcal mol^{-1}. $E_{a,r}$ = 5.45 kcal mol^{-1}. (taken from the same reference).

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{12}$ = 1/2 (H + C=C), NIST. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (22.89) kcal mol^{-1}. $E_{a,r}$ = 2.7 kcal mol^{-1}. (estimated by Bozzelli).

IID. 63 C_2H_2 + OH → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	$C_2H_2 + OH \rightarrow C.=COH$	5.12×10^{12} T^0 e^{-0T}	1.40
k_{-1}	$C.=COH \rightarrow C_2H_2 + OH$	3.18×10^{13} T^0 e^{-0T}	33.41
k_2	$C.=COH \rightarrow C\equiv COH + H$	3.99×10^{12} T^0 e^{-0T}	45.49
k_3	$C.=COH \rightarrow C=CO.$	2.06×10^{12} $T^{0.1}$ $e^{-0.00087T}$	30.73
k_{-3}	$C=CO. \rightarrow C.=COH$	1.13×10^{10} $T^{1.0}$ e^{-0T}	54.03
k_4	$C=CO. \rightarrow C=C=O + H$	1.42×10^{12} T^0 e^{-0T}	36.68
k_5	$C=CO. \rightarrow C.CHO$	3.60×10^{16} T^0 e^{-0T}	0.00
k_{-5}	$C.CHO \rightarrow C=CO.$	3.66×10^{16} T^0 e^{-0T}	3.18
k_6	$C.CHO \rightarrow CH_3C.=O$	6.50×10^{9} $T^{1.0}$ e^{-0T}	35.00
k_{-6}	$CH_3C.=O \rightarrow C.CHO$	2.38×10^{7} $T^{2.2}$ $e^{-0.00065T}$	40.92
k_7	$CH_3C.=O \rightarrow CH_3 + CO$	2.05×10^{12} T^0 e^{-0T}	13.35
k_8	$CH_3C.=O \rightarrow C=C=O + H$	4.33×10^{12} T^0 e^{-0T}	44.28

frequency/degeneracy (CPFIT)
C.=COH: 504.0 (3.819); 1135.7 (4.866); 3449.5 (2.815)

C=CO.: 578.8 (3.802); 1311.9 (5.098); 3085.1 (3.100)
C.CHO: 556.8 (3.618); 1205.4 (4.219); 2442.0 (3.663)
CH3C.=O: 485.8 (3.061); 1486.0 (5.839); 2844.5 (2.600)
Lennard-Jones parameter
σ(Å) = 4.35, ε/k (K) = 422.61

k_1 88 LIU/MUL2.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f}$ (1.4) - ΔU_{rxn} (-32.01) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.79 \times 10^{12}$, 72 WAG for CC≡C + H → C.=CC. $E_{a,f} = E_{a,r}$ (3.1) + ΔU_{rxn} (42.39) kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (-23.3) kcal mol^{-1}.

k_{-3} A_r estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of rotors (no rotor loss here, $\Delta S^{\neq}(T) = 0$). $E_{a,f}$ = RS (26) + E_{abst} (4.73) + ΔH_{rxn} (23.3) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 7.00 \times 10^{12}$, 84 WAR for C=C=O + H → Prod.. $E_{a,f} = E_{a,r}$ (3.011) + ΔU_{rxn} (33.67) kcal mol^{-1}.

k_5 Jeff Ing. PHD thesis.

k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-3.18) kcal mol^{-1}.

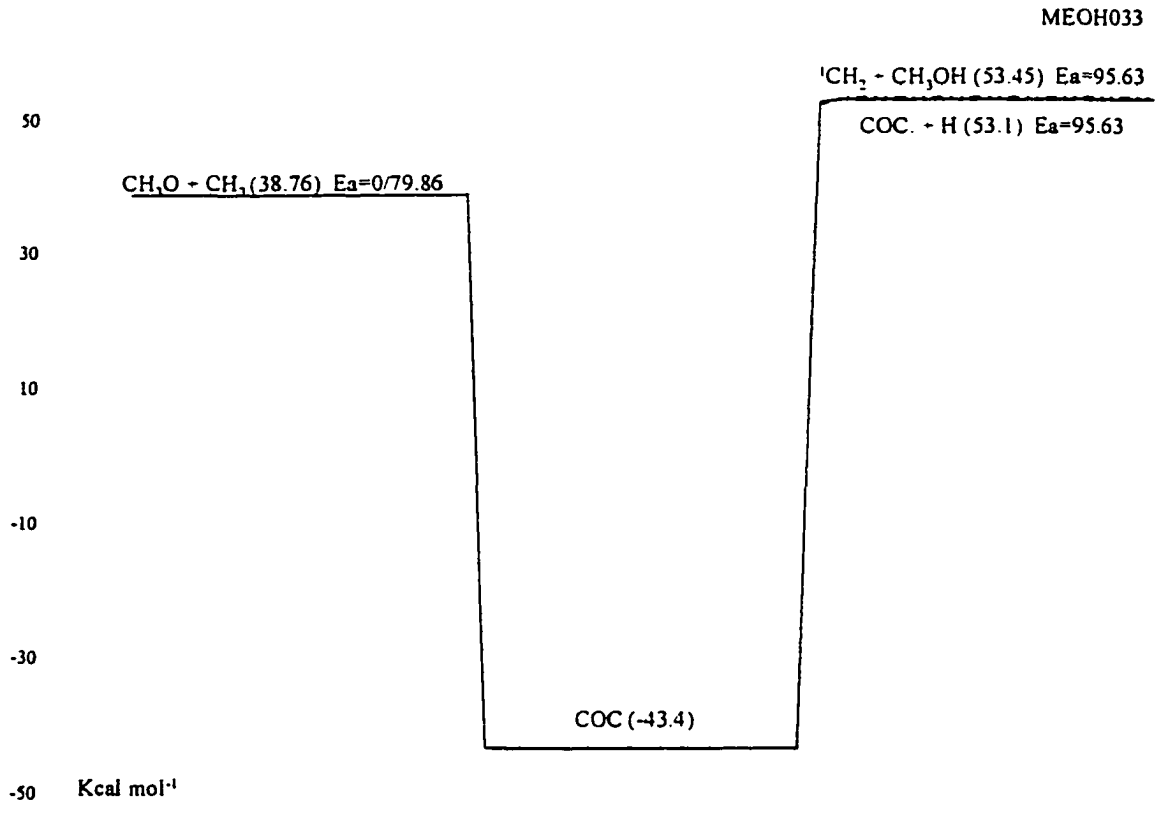
k_6 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f}$ = RS (28) + E_{abst} (7.0) kcal mol^{-1}.

k_{-6} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-5.92) kcal mol^{-1}.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{11}$,86 TSA/HAM for CC. + CO → CCC.=O, $E_{a,f} = E_{a,r}$ (4.809) + ΔU_{rxn} (8.54) kcal mol^{-1}.

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{13}$,84 WAR for C=C + H, $E_{a,f} = E_{a,r}$ (1.506) + ΔU_{rxn} (42.77) kcal mol^{-1}.

IID. 64 COC → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	$CH_3O + CH_3 \rightarrow COC$	1.21×10^{13} T^0 e^{-0T}	0.00
k_{-1}	$COC \rightarrow CH_3O + CH_3$	8.14×10^{15} T^0 e^{-0T}	79.86
k_2	$COC \rightarrow COC. + H$	5.60×10^{15} T^0 e^{-0T}	96.13
k_3	$COC \rightarrow CH_2S + CH_3OH$	2.16×10^{16} T^0 e^{-0T}	95.63

frequency/degeneracy (CPFIT)
COC: 635.8 (7.937); 1878.7 (9.590); 3509.4 (2.473)
Lennard-Jones parameter
σ(Å) = 4.34, ε/k (K) = 422.61

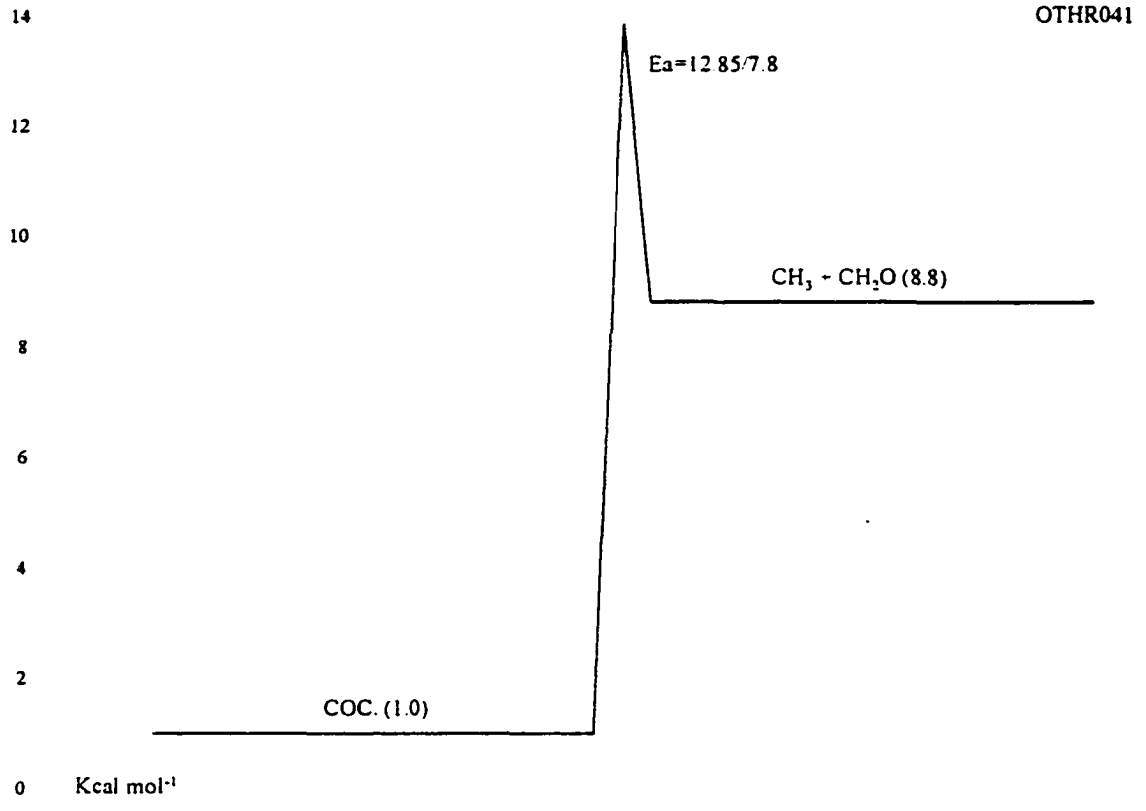
k_1 86 TSA/HAM.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-79.86) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.00 \times 10^{13} = 2 \times$ (H + CH_2OH), 81 HOY/COF. $E_{a,f} = E_{a,r}$ (0) + ΔU_{rxn} (96.13) kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.50 \times 10^{13}$, Jeff Ing. PHD THESIS. $E_{a,f} = E_{a,r}$ (1.0) + ΔU_{rxn} (94.63) kcal mol^{-1}.

IID. 65 COC. → $CH_2O + CH_3$

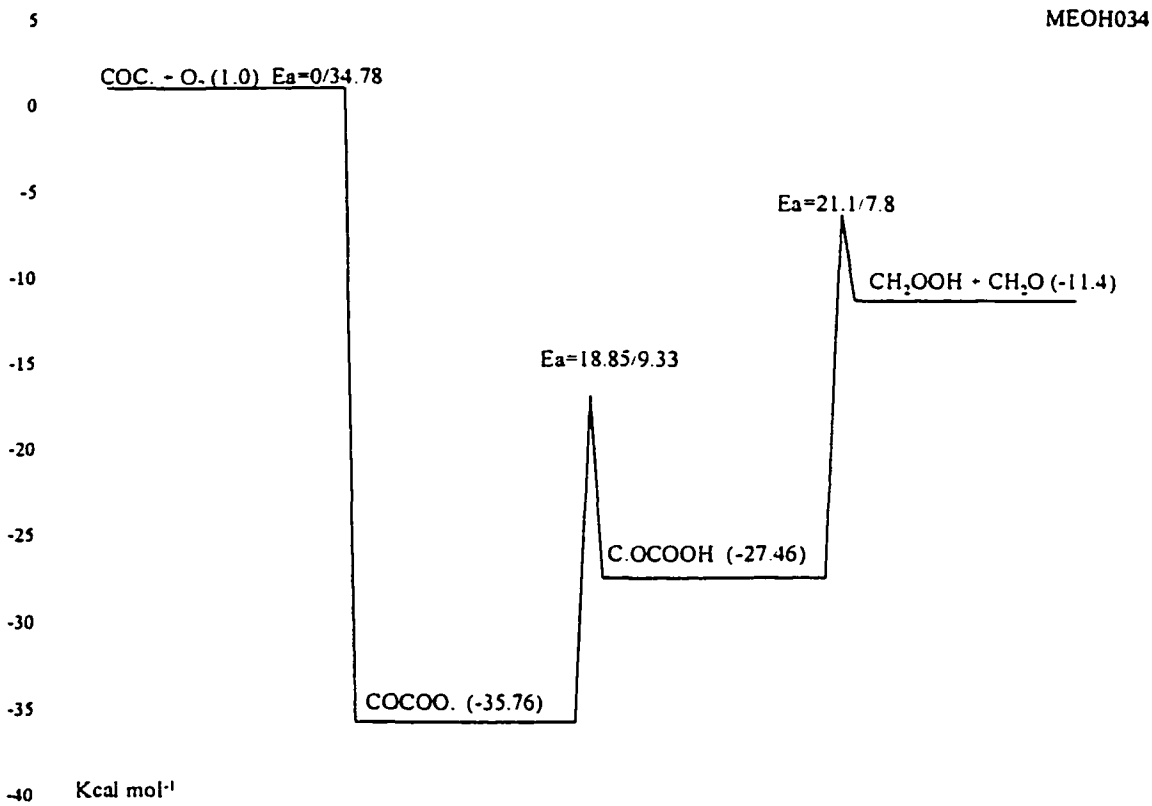


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	COC. → $CH_2O + CH_3$	3.69×10^{12} T^0 e^{-0T}	12.85

frequency/degeneracy (CPFIT)
COC.: 516.9 (6.322); 1262.4 (3.723); 2460.9 (6.954)
Lennard-Jones parameter
σ(Å) = 4.35, ε/k (K) = 422.61

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.31 \times 10^{11}$ 86 TSA/HAM for $CH_3 + C{=}C$. $E_{a,f} = E_{a,r}$ (7.8) + ΔU_{rxn} (5.05) kcal mol^{-1}.

IID. 66 COC. + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	COC. + O_2 → COCOO.	6.00×10^{12} T^0 e^{-0T}	0.00
k_{-1}	COCOO. → COC. + O_2	8.52×10^{13} T^0 e^{-0T}	34.78
k_2	COCOO. → C.OCOOH	5.15×10^{8} $T^{1.0}$ e^{-0T}	18.85
k_{-2}	C.OCOOH → COCOO.	2.07×10^{13} $T^{-1.01}$ $e^{-0.0011T}$	9.33
k_3	C.OCOOH → CH_2O + CH_2OOH	6.66×10^{12} T^0 e^{-0T}	21.10

frequency/degeneracy (CPFIT)
COCOO.: 366.7 (7.587); 800.0 (3.436); 2104.7 (11.478)
C.OCOOH: 450.0 (9.178); 473.6 (3.020); 1959.6 (9.802)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 2 × (CC. + O_2), 89 ATK/BAU and 90 DEM/SAN.

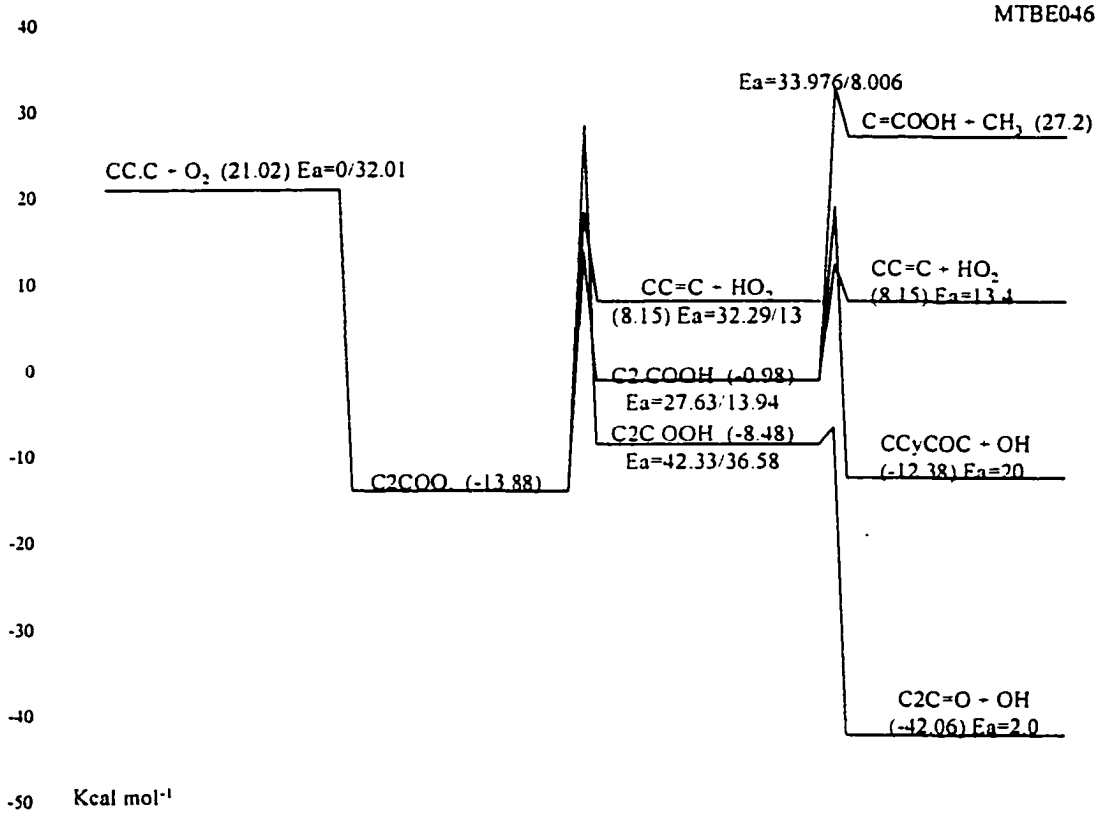
k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-34.78) kcal mol^{-1}.

k_2 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 3, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (0) + E_{abst} (9.33) + ΔH_{rxn} (9.52) kcal mol^{-1}.

k_{-2} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (9.52) kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.31 \times 10^{11}$, 86 TSA/HAM and 72 KER/PAR for C=C + CH_3. $E_{a,f} = E_{a,r}$ (7.8) + ΔU_{rxn} (13.30) kcal mol^{-1}.

IID. 67 CC.C + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC.C + O_2 → C2COO.	6.62×10^{12} T^0 e^{-0T}	0.00
k_{-1}	C2COO. → CC.C + O_2	1.41×10^{15} T^0 e^{-0T}	32.01
k_2	C2COO. → CC=C + HO_2	4.98×10^{9} $T^{1.18}$ e^{-0T}	32.29
k_3	C2COO. → C2C.OOH	1.30×10^{10} $T^{1.0}$ e^{-0T}	42.33
k_{-3}	C2C.OOH → C2COO.	1.33×10^{11} $T^{0.04}$ $e^{-0.00073T}$	36.58
k_4	C2C.OOH → C2C=O + OH	4.48×10^{12} T^0 e^{-0T}	2.00
k_5	C2COO. → C2.COOH	5.27×10^{9} $T^{1.08}$ e^{-0T}	27.63
k_{-5}	C2.COOH → C2COO.	1.32×10^{11} $T^{-0.04}$ $e^{-0.00052T}$	13.94
k_6	C2.COOH → CCyCOC + OH	6.80×10^{11} $T^{-0.27}$ e^{-0T}	20.00
k_7	C2.COOH → CC=C + HO_2	4.56×10^{12} $T^{-0.14}$ e^{-0T}	13.41
k_8	C2.COOH → C=COOH + CH_3	1.55×10^{12} T^0 e^{-0T}	33.98

frequency/degeneracy (CPFIT)
C2COO.: 250.0 (7.189); 1111.8 (12.877); 2859.1 (8.434)
C2C.OOH: 100.3 (7.507); 1069.9 (12.133); 2730.8 (8.360)

Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 92 ATK/BAU

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (32.01) kcal mol^{-1}.

k_2 A_f calculated by Bozzelli based on TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, with $\Delta S^{\neq}(T)$ from MOPAC calculation, $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (19.29) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_3 A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1 ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain of an optical isomer (OI), $E_{a,f}$ = RS (26) + E_{abst} (10.58) + ΔH_{rxn} (5.75) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (5.75) kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.0 kcal mol^{-1} based on $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_5 A_f calculated by Bozzelli based on TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, with $\Delta S^{\neq}(T)$ from MOPAC calculation, $E_{a,f}$ = RS (6) + E_{abst} (7.94) + ΔH_{rxn} (13.69) kcal mol^{-1}.

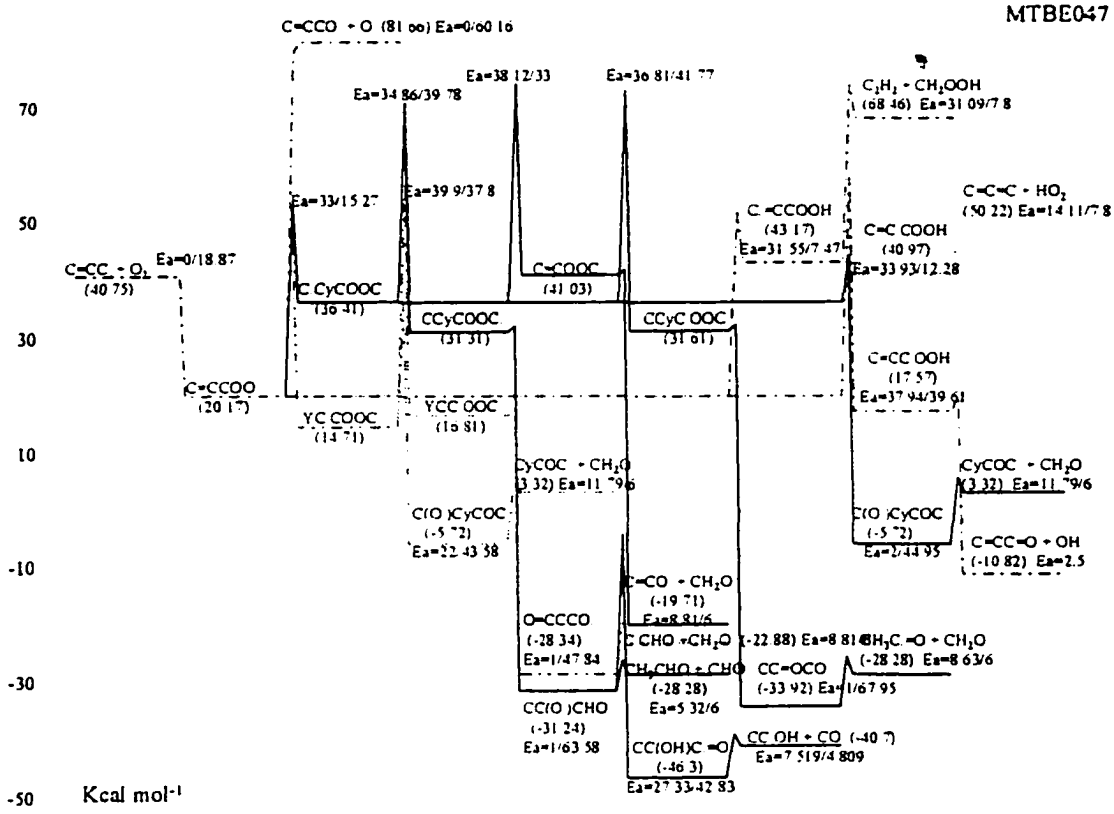
k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (13.69) kcal mol^{-1}.

k_6 A_f calculated by Bozzelli based on TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, with $\Delta S^{\neq}(T)$ from MOPAC calculation, $E_{a,f}$ is evaluated in this study.

k_7 A_f calculated by Bozzelli based on TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, with $\Delta S^{\neq}(T)$ from MOPAC calculation, $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (7.88) kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for $C_3H_6 + CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 25.97 kcal mol^{-1}. $E_{a,r}$ = 8.006 kcal mol^{-1}. (referenced as the same as the A_r).

IID. 68 C=CC. + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C=CC. + O_2 → C=CCOO.	3.61×10^{11} T^0 e^{-0T}	0.00
k_{-1}	C=CCOO. → C=CC. + O_2	2.83×10^{12} T^0 e^{-0T}	18.87
k_2	C=CCOO. → C=CCO. + O	1.85×10^{14} T^0 e^{-0T}	60.16
k_3	C=CCOO. → C=CC.OOH	2.60×10^{10} $T^{1.0}$ e^{-0T}	37.94
k_{-3}	C=CC.OOH → C=CCOO.	2.27×10^{13} $T^{-0.18}$ $e^{-0.00007T}$	39.61
k_4	C=CC.OOH → C=CCHO + OH	1.48×10^{14} T^0 e^{-0T}	2.50
k_5	C=CCOO. → C=C.COOH	1.50×10^{9} $T^{1.0}$ e^{-0T}	33.93
k_{-5}	C=C.COOH → C=CCOO.	4.39×10^{11} $T^{-0.16}$ $e^{-0.0005T}$	12.28
k_6	C=C.COOH → C=C=C + HO_2	1.68×10^{12} T^0 e^{-0T}	14.11
k_7	C=CCOO. → C.=CCOOH	2.99×10^{9} $T^{1.0}$ e^{-0T}	31.55
k_{-7}	C.=CCOOH → C=CCOO.	6.94×10^{12} $T^{-0.49}$ $e^{-0.00065T}$	7.47
k_8	C.=CCOOH → C_2H_2 + CH_2OOH	1.98×10^{13} T^0 e^{-0T}	31.09
k_9	C=CCOO. → CyC.COOC	4.68×10^{11} T^0 e^{-0T}	31.60
k_{-9}	CyC.COOC → C=CCOO.	2.62×10^{13} T^0 e^{-0T}	35.24
k_{10}	CyC.COOC → CyCOC(CO.)	1.00×10^{13} T^0 e^{-0T}	22.00

	Reaction	A $T^n e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_{-10}	CyCOC(CO.) → CyC.COOC	3.89×10^{12} T^0 e^{-0T}	43.58
k_{11}	CyCOC(CO.) → CCyCC.OOC	1.76×10^{13} T^0 e^{-0T}	11.79
k_{12}	CyC.COOC → CyCC.OOC	2.26×10^{11} $T^{1.0}$ e^{-0T}	39.90
k_{-12}	CyCC.OOC → CyC.COOC	4.53×10^{11} $T^{1.0}$ e^{-0T}	37.80
k_{13}	CyCC.OOC → O=CCCO.	3.54×10^{13} T^0 e^{-0T}	1.00
k_{-13}	O=CCCO. → CyCC.OOC	4.68×10^{11} T^0 e^{-0T}	47.84
k_{14}	O=CCCO. → C.CHO + CH_2O	1.28×10^{12} T^0 e^{-0T}	8.81
k_{15}	C=CCOO. → C.CyCOOC	4.68×10^{11} T^0 e^{-0T}	33.00
k_{-15}	C.CyCOOC → C=CCOO.	8.27×10^{12} T^0 e^{-0T}	15.27
k_{16}	C.CyCOOC → C=COOC.	5.49×10^{12} T^0 e^{-0T}	38.12
k_{-16}	C=COOC.→ C.CyCOOC	5.38×10^{10} T^0 e^{-0T}	33.00
k_{17}	C=COOC.→ C=CO. + CH_2O	1.53×10^{13} T^0 e^{-0T}	1.00
k_{18}	C.CyCOOC → CyCOC(CO.)	4.08×10^{12} T^0 e^{-0T}	8.00
k_{-18}	CyCOC(CO.) → C.CyCOOC	5.02×10^{12} T^0 e^{-0T}	50.95
k_{19}	CyCOC(CO.) → CyCOC. + CH_2O	1.76×10^{13} T^0 e^{-0T}	11.79
k_{20}	C.CyCOOC → CCyC.OOC	6.50×10^{9} $T^{1.0}$ e^{-0T}	36.87
k_{-20}	CCyC.OOC → C.CyCOOC	1.43×10^{10} $T^{1.0}$ $e^{-0.00009T}$	41.77
k_{21}	CCyC.OOC → CC(=O)CO.	4.96×10^{13} T^0 e^{-0T}	1.00
k_{-21}	CC(=O)CO. → CCyC.OOC	4.08×10^{12} T^0 e^{-0T}	67.95
k_{22}	CC(=O)CO. → $CH_3C.=O$ + CH_2O	1.00×10^{13} T^0 e^{-0T}	8.63
k_{23}	C.CyCOOC → CCyCOOC.	1.30×10^{10} $T^{1.0}$ e^{-0T}	34.86
k_{-23}	CCyCOOC. → C.CyCOOC	1.17×10^{12} $T^{0.46}$ $e^{-0.00041T}$	39.78
k_{24}	CCyCOOC. → CC(O.)CHO	8.09×10^{13} T^0 e^{-0T}	1.00
k_{-24}	CC(O.)CHO → CCyCOOC.	4.08×10^{12} T^0 e^{-0T}	64.58
k_{25}	CC(O.)CHO → CH_3CHO + CHO	9.16×10^{12} T^0 e^{-0T}	5.32
k_{26}	CC(O.)CHO → C2C(OH)C.=O	6.50×10^{9} $T^{1.0}$ e^{-0T}	27.33
k_{-26}	C2C(OH)C.=O → CC(O.)CHO	1.49×10^{9} $T^{1.01}$ $e^{-0.00038T}$	42.83
k_{27}	C2C(OH)C.=O → C2C=O + CHO	3.28×10^{12} T^0 e^{-0T}	7.52

frequency/degeneracy (CPFIT)

C=CCOO.: 250.2 (6.265); 1062.0 (9.404); 2787.9 (7.331)
C=CC.OOH: 250.2 (6.237); 1049.3 (10.657); 2504.4 (5.606)
C=C.COOH: 250.1 (7.596); 1156.5 (9.768); 2748.4 (5.136)
C.=CCOOH: 251.1 (7.383); 1087.0 (9.979); 2746.1 (5.138)
CyC.COOC: 250.1 (3.158); 1034.0 (16.543); 2708.5 (4.299)
CyCOC(CO.): 250.9 (3.423); 1006.8 (14.393); 2896.7 (5.684)
CyCC.OOC: 250.1 (3.158); 1034.0 (16.543); 2708.5 (4.299)
O=CCCO.: 513.3 (10.877); 1805.9 (9.913); 3999.6 (2.210)
C.CyCOOC: 250.7 (2.831); 959.2 (14.424); 2187.3 (6.245)
C=COOC.: 510.4 (12.353); 1463.5 (8.291); 3296.4 (1.857)
CCyC.OOC: 251.4 (3.448); 967.9 (13.280); 2172.2 (6.773)
CC(=O)CO.: 469.2 (9.796); 1694.2 (9.877); 3139.4 (3.327)

CCyCOOC.: 250.0 (3.140); 964.1 (15.134); 2436.5 (5.226)
CC(O.)CHO: 251.8 (5.080); 1041.8 (12.047); 2706.1 (5.874)
CC(OH)C.=O: 250.3 (5.384); 1058.9 (11.400); 2797.0 (5.716)
Lennard-Jones parameter
σ(Å) = 5.86, ε/k (K) = 632.06

k_1 93 JEN/MUR

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -18.87 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 92 BAU/COB for ($CH_3O + O \rightarrow$ Prod.. $E_{a,f} = \Delta U_{rxn}$ = 60.16 kcal mol^{-1}.

k_3 A_r estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 2 ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 kcal mol^{-1}) and gain of an optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (11.94) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -1.67 kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_5 A_r estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1 ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 kcal mol^{-1}) and gain of an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (6.28) + ΔH_{rxn} (21.65) kcal mol^{-1}.

k_{-5} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 21.65 kcal mol^{-1}.

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.50 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 6.31 kcal mol^{-1}. $E_{a,r}$ = 7.80 kcal mol^{-1}. (estimated by Bozzelli).

k_7 A_r estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 2 ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 kcal mol^{-1}) and gain of an optical isomer (OI). $E_{a,f}$ = RS (0) + E_{abst} (7.47) kcal mol^{-1} + ΔH_{rxn} (24.08) kcal mol^{-1}.

k_{-7} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 24.08 kcal mol^{-1}.

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.01 \times 10^{11}$ =1/2 (C≡C + CH_3), 92 BAU/COB. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 23.29 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_9 A_r estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_bT/h = $10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is estimated by Bozzelli.

k_{-9} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -3.64 kcal mol^{-1}.

k_{10} A_f is taken from ref [55]. $E_{a,f}$ is estimated as the difference of ring strain (28 - 6) kcal mol^{-1}.

k_{-10} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -21.58 kcal mol^{-1}.

k_{11} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.08 \times 10^{11}$, 88 TSA for CH_2O + CC.C → CCC + CHO. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 5.79 kcal mol^{-1}. $E_{a,r}$ = 6.0 kcal mol^{-1}. (estimated by Bozzelli).

k_{12} A_r estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1 $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of rotor (no rotor loss here, so $\Delta S^{\neq}(T) = 0$), $E_{a,f}$ = RS (0) + E_{abst} (9.80) + ΔH_{rxn} (2.10) kcal mol^{-1}.

k_{-12} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 2.10 kcal mol^{-1}.

k_{13} A_f via A_r and Microscopic Reversbility (MR), $E_{a,f}$ is estimated as 1 kcal mol^{-1} by Bozzelli.

k_{-13} A_r estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -46.84 kcal mol^{-1}.

k_{14} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.58 \times 10^{11}$, 72 KER/PAR for CC. + C=C → CCCC.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 2.81 kcal mol^{-1}. $E_{a,r}$ = 6.0 kcal mol^{-1}. (estimated by Bozzelli).

k_{15} A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is estimated as ring strain (26) + $E_{a,add}$ (7).

k_{-15} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 17.73 kcal mol^{-1}.

k_{16} A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 5.12 kcal mol^{-1}.

k_{-16} A_r estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}). $E_{a,r}$ is estimated as ring strain (26) + $E_{a,add}$ (7).

k_{17} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.60 \times 10^{11}$, NIST fit for CH_3O + CO. $E_{a,f}$ is estimated as 1.0 kcal mol^{-1} by Bozzelli.

k_{18} A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,f}$ is estimated by Bozzelli.

k_{-18} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -42.95 kcal mol^{-1}.

k_{19} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.08 \times 10^{11}$, 88 TSA for CH_2O + CC.C → CCC + CHO. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 5.79 kcal mol^{-1}. $E_{a,r}$ = 6.0 kcal mol^{-1}. (estimated by Bozzelli).

k_{20} A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1 $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}), $E_{a,f}$ = RS (28) + E_{abst} (8.87) kcal mol^{-1}.

k_{-20} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -4.90 kcal mol^{-1}.

k_{21} A_f via A_r and Microscopic Reversbility (MR), $E_{a,f}$ is estimated as 1.0 kcal mol^{-1} by

Bozzelli.

k_{-21} A_r estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -66.95 kcal mol^{-1}.

k_{22} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.08 \times 10^{11}$, 88 TSA for CH_2O + CC.C → CCC + CHO. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 2.63 kcal mol^{-1}. $E_{a,r}$ = 6.0 kcal mol^{-1}. (estimated by Bozzelli).

k_{23} A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1 $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}), $E_{a,f}$ = RS (26) + E_{abst} (8.86) kcal mol^{-1}.

k_{-23} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -4.92 kcal mol^{-1}.

k_{24} A_f via A_r and Microscopic Reversbility (MR), $E_{a,f}$ is estimated as 1.0 kcal mol^{-1} by Bozzelli.

k_{-24} A_r estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}). $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -63.58 kcal mol^{-1}.

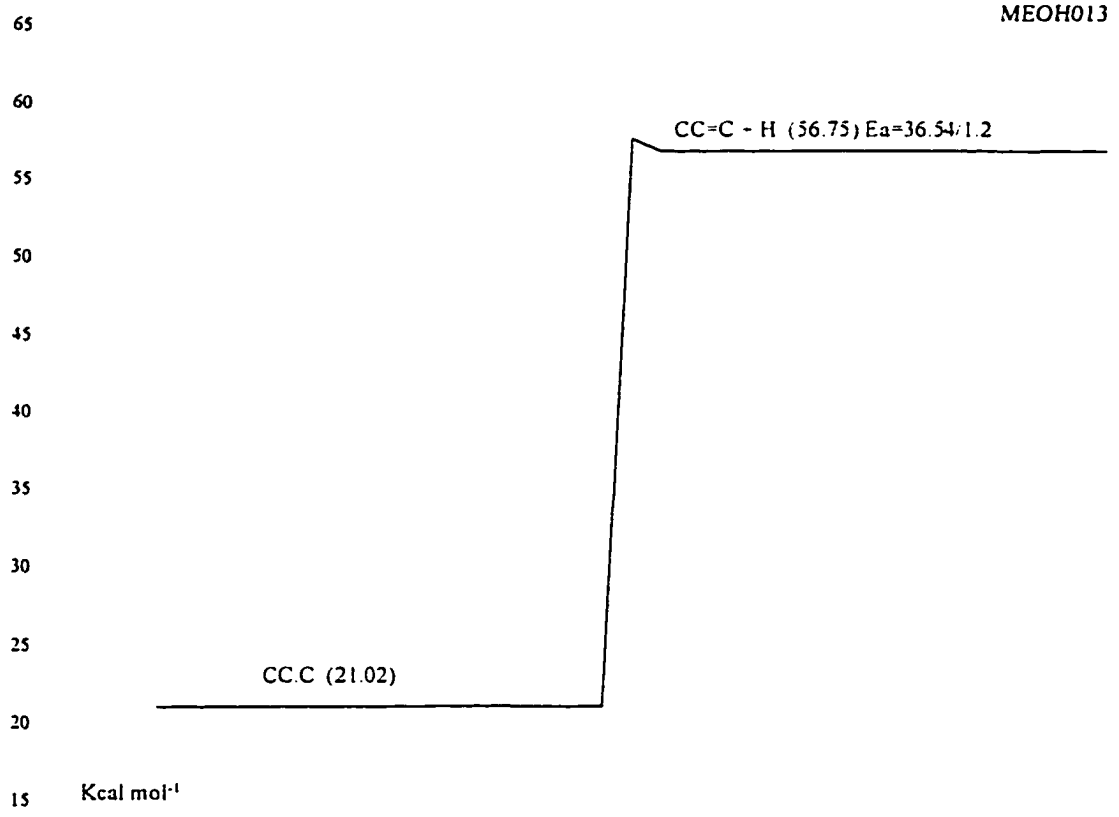
k_{25} A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.01 \times 10^{11}$ =1/2 (CC=C + CHO → Prod.), NIST. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = -0.68 kcal mol^{-1}. $E_{a,r}$ = 6.0 kcal mol^{-1}. (estimated by Bozzelli).

k_{26} A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1 $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}), $E_{a,f}$ = RS (26) + E_{abst} (1.33) kcal mol^{-1}.

k_{-26} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -15.50 kcal mol^{-1}.

k_{27} A_f via A_r and Microscopic Reversbility (MR), $A_r = 7.50 \times 10^{10}$ =1/2 (CC. + CO), 86 TSA/HAM. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 2.71 kcal mol^{-1}. $E_{a,r}$ = 4.809 kcal mol^{-1}. (taken from the same reference as A_r).

IID. 69 CC.C → CC=C + H

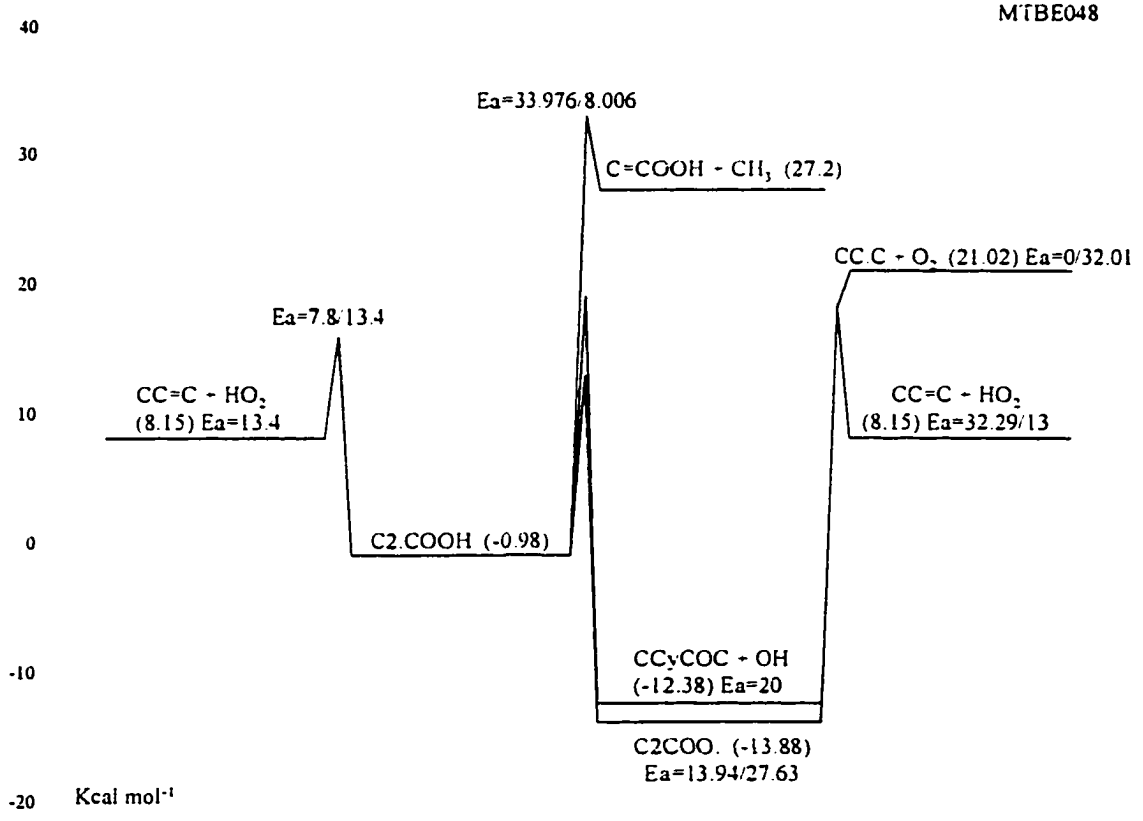


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC.C → CC=C + H	7.78×10^{12} T^0 e^{-0T}	36.54

frequency/degeneracy (CPFIT)
CC.C: 554.4 (6.897); 1622.0 (11.862); 3563.2 (4.241)
Lennard-Jones parameter
σ(Å) = 4.98, ε/k (K) = 266.8

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 7.24 \times 10^{12}$, 72 KER/PAR. $E_{a,f} = E_{a,r}$ (1.2) + ΔU_{rxn} (36.54) kcal mol^{-1}.

IID. 70 CC=C + HO_2 → [C2C.OOH]$^{\cdot}$ → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC=C + HO_2 → C2.COOH	2.13×10^{4} $T^{2.44}$ $e^{0.00014T}$	7.80
k_{-1}	C2.COOH → CC=C + HO_2	4.56×10^{12} $T^{-0.14}$ e^{-0T}	13.40
k_2	C2.COOH → CCyCOC + OH	6.80×10^{11} $T^{-0.27}$ e^{-0T}	20.00
k_3	C2.COOH → C=COOH + CH_3	1.55×10^{12} T^{0} e^{-0T}	33.98
k_4	C2.COOH → C2COO.	1.32×10^{11} $T^{-0.04}$ $e^{-0.00052T}$	13.94
k_{-4}	C2COO. → C2.COOH	5.27×10^{9} $T^{1.08}$ e^{-0T}	27.63
k_5	C2COO. → CC=C + HO_2	4.98×10^{9} $T^{1.18}$ e^{-0T}	32.29
k_6	C2COO. → CC.C + O_2	1.41×10^{15} T^{0} e^{-0T}	32.01

frequency/degeneracy (CPFIT)
C2C.OOH: 100.3 (7.507); 1069.9 (12.133); 2730.8 (8.360)
C2COO.: 250.0 (7.189); 1111.8 (12.877); 2859.1 (8.434)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f}$ estimated by Bozzelli.

k_{-1} A_r calculated by Bozzelli based on TST with MOPAC, $E_{a,r} = E_{a,f} - \Delta U_{rxn}$ (-32.01) kcal mol^{-1}.

k_2 A_f calculated by Bozzelli based on TST, $A = (deg.)\ (ek_bT/h)\ \exp(\Delta S^{\neq}(T)/R)$, with $\Delta S^{\neq}(T)$ from MOPAC calculation, $E_{a,f}$ is evaluated in this study.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for $C_3H_6 + CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, $\Delta U_{rxn} = 25.97$ kcal mol^{-1}. $E_{a,r} = 8.006$ kcal mol^{-1}. (referenced as the same as the A_r).

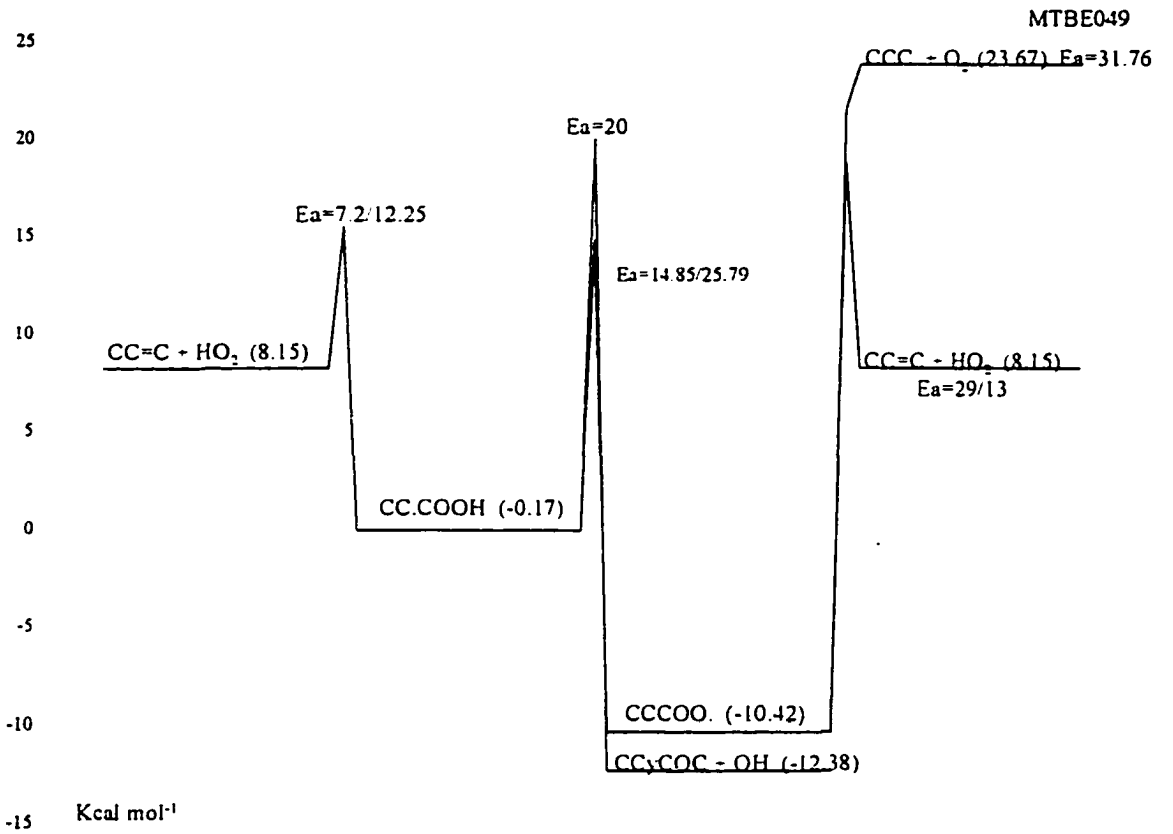
k_4 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (-5.75) kcal mol^{-1}.

k_{-4} A_r calculated by Bozzelli based on TST, $A = (deg.)\ (ek_bT/h)\ \exp(\Delta S^{\neq}(T)/R)$, with $\Delta S^{\neq}(T)$ from MOPAC calculation, $E_{a,r}$ = RS (26) + E_{abst} (10.58) + ΔH_{rxn} (5.75) kcal mol^{-1}.

k_5 A_f calculated by Bozzelli based on TST, $A = (deg.)\ (ek_bT/h)\ \exp(\Delta S^{\neq}(T)/R)$, with $\Delta S^{\neq}(T)$ from MOPAC calculation, $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (19.29) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.62 \times 10^{12}$, 92 ATK/BAU. $E_{a,f} = \Delta U_{rxn} = 32.01$ kcal mol^{-1}.

IID. 71 CC=C + HO_2 → [CC.COOH]* → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC=C + HO_2 → CC.COOH	5.01×10^{11} T^0 e^{-0T}	7.20
k_{-1}	CC.COOH → CC=C + HO_2	6.69×10^{12} T^0 e^{-0T}	12.25
k_2	CC.COOH → CCyCOC + OH	4.68×10^{11} T^0 e^{-0T}	20.00
k_3	CC.COOH → CCCOO.	9.16×10^{10} $T^{0.01}$ $e^{-0.00047T}$	14.85
k_{-3}	CCCOO. → CC.COOH	1.50×10^{9} T^0 e^{-0T}	25.79
k_4	CCCOO. → CC=C + HO_2	7.47×10^{9} $T^{0.73}$ e^{-0T}	29.00
k_5	CCCOO. → CCC. + O_2	5.74×10^{14} T^0 e^{-0T}	31.76

frequency/degeneracy (CPFIT)
CC.COOH: 250.3 (8.681); 1245.6 (12.964); 2818.4 (6.355)
CCCOO.: 251.0 (7.429); 1148.5 (12.338); 2789.4 (8.734)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.01 \times 10^{11}$, 72 KER/PAR for C=C + $HO_2 \rightarrow$ Prod.. $E_{a,f}$ is estimated by Bozzelli.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -5.05 kcal mol^{-1}.

k_2 A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

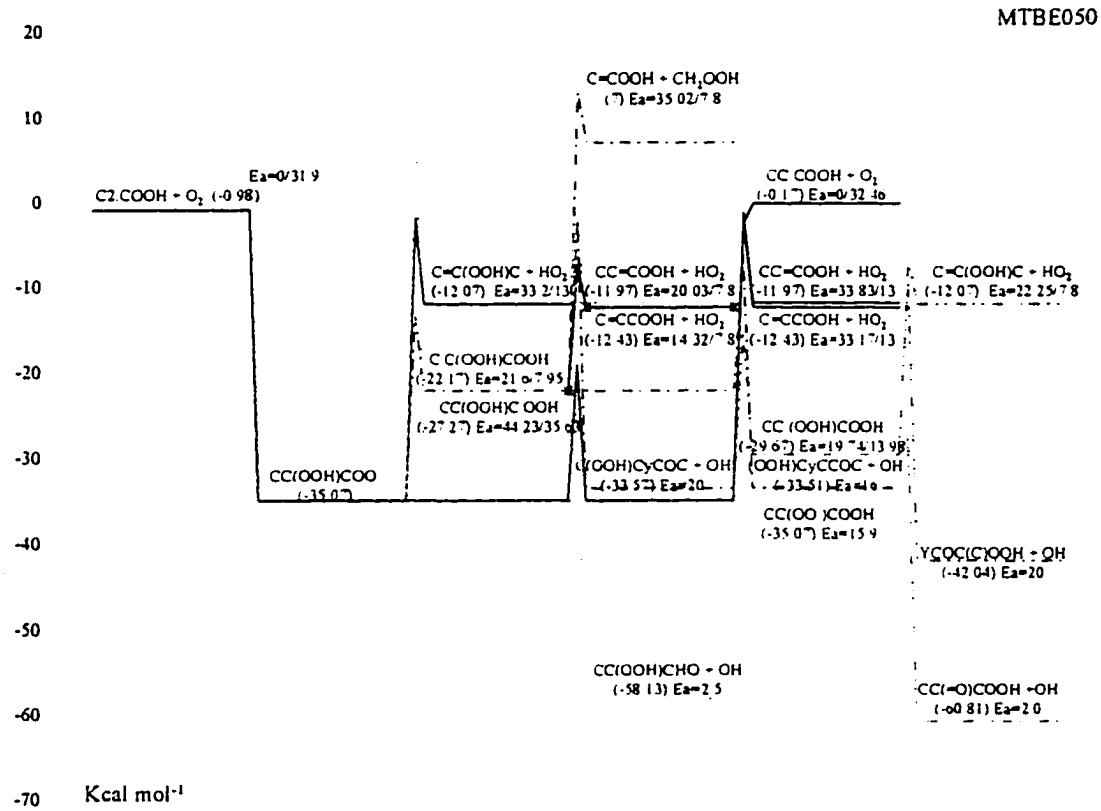
k_3 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (-10.94) kcal mol^{-1}.

k_{-3} A_r estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1 $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}) and gain of an optical isomer (OI), $E_{a,r}$ = RS (6) + E_{abst} (8.85) + ΔH_{rxn} (10.94) kcal mol^{-1}.

k_4 A_f is referenced from reaction C2CCOO. $\rightarrow$ C2C=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (16.0) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.01 \times 10^{12}$, NIST fit for CC. + O_2. $E_{a,f} = \Delta U_{rxn}$ = 32.01 kcal mol^{-1}.

IID. 72 C2.COOH + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2.COOH + O_2 → CC(OOH)COO.	1.00×10^{12} T^0 e^{-0T}	0.00
k_{-1}	CC(OOH)COO. → C2.COOH + O_2	1.04×10^{14} T^0 e^{-0T}	31.90
k_2	CC(OOH)COO. → C=C(OOH)C + HO_2	7.48×10^{9} $T^{0.73}$ e^{-0T}	33.20
k_3	CC(OOH)COO. → CC(OOH)C.OOH	2.60×10^{10} $T^{1.0}$ e^{-0T}	44.23
k_{-3}	CC(OOH)C.OOH → CC(OOH)COO.	6.81×10^{12} $T^{-0.33}$ $e^{-0.00073T}$	35.63
k_4	CC(OOH)C.OOH → CC(OOH)CHO + OH	3.21×10^{13} T^0 e^{-0T}	2.50
k_5	CC(OOH)C.OOH → CC=COOH + HO_2	1.48×10^{12} T^0 e^{-0T}	20.03
k_6	CC(OOH)COO. → C.C(OOH)COOH	5.15×10^{8} $T^{1.0}$ e^{-0T}	21.60
k_{-6}	C.C(OOH)COOH → CC(OOH)COO.	2.43×10^{10} $T^{-0.12}$ $e^{-0.00054T}$	7.95
k_7	C.C(OOH)COOH → CyCOC(COOH) + OH	4.68×10^{11} T^0 e^{-0T}	20.00
k_8	C.C(OOH)COOH → C=CCOOH + HO_2	4.82×10^{12} T^0 e^{-0T}	14.32
k_9	C.C(OOH)COOH → C=COOH + CH_2OOH	4.93×10^{12} T^0 e^{-0T}	35.02
k_{10}	C.C(OOH)COOH → CyCCOC(OOH) + OH	5.38×10^{10} T^0 e^{-0T}	16.00
k_{11}	CC(OOH)COO. → CC.(OOH)COOH	1.50×10^{9} $T^{1.0}$ e^{-0T}	19.74
k_{-11}	CC.(OOH)COOH → CC(OOH)COO.	1.47×10^{10} $T^{0.04}$ $e^{-0.00072T}$	13.98

	Reaction	A $T^n e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_{12}	CC.(OOH)COOH → CC(=O)COOH + OH	8.71×10^{12} T^0 e^{-0T}	2.00
k_{13}	CC.(OOH)COOH → CyCOC(C)OOH + OH	4.68×10^{11} T^0 e^{-0T}	20.00
k_{14}	CC.(OOH)COOH → C=C(OOH)C + HO_2	2.94×10^{12} T^0 e^{-0T}	22.25
k_{15}	CC(OOH)COO. → CC(OO.)COOH	9.85×10^{6} $T^{1.0}$ e^{-0T}	15.90
k_{-15}	CC(OO.)COOH → CC(OOH)COO.	9.85×10^{6} $T^{1.0}$ e^{-0T}	15.90
k_{16}	CC(OO.)COOH → CC.COOH + O_2	4.90×10^{14} T^0 e^{-0T}	32.46
k_{17}	CC(OO.)COOH → C=CCOOH + HO_2	2.49×10^{9} $T^{1.18}$ e^{-0T}	33.17
k_{18}	CC(OO.)COOH → CC=COOH + HO_2	1.66×10^{9} $T^{1.18}$ e^{-0T}	33.83

frequency/degeneracy (CPFIT)
CC(OOH)COO.: 100.1 (10.107); 1059.7 (15.280); 2808.7 (8.113)
CC(OOH)C.OOH: 100.1 (11.462); 1084.1 (14.972); 2766.1 (6.566)
C.C(OOH)COOH: 100.0 (10.777); 1065.9 (15.825); 2784.7 (6.397)
CC.(OOH)COOH: 100.2 (11.914); 1126.4 (13.906); 2772.2 (7.180)
CC(OO.)COOH: 100.1 (10.107); 1059.7 (15.280); 2808.7 (8.113)
Lennard-Jones parameter
σ(Å) = 5.86, ε/k (K) = 632.06

k_1 taken from 88 XI for C3CC. + O_2.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -31.9 kcal mol^{-1}.

k_2 A_f is referenced from reaction C2CCOO. → C2C=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (20.2) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_3 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (9.63) + ΔH_{rxn} (8.60) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 8.60 kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75\times10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.5\times10^{11}$ = 1/2(C=C + HO_2), 72 KER/PAR. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 12.23 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_6 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 3, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (0) + E_{abst} (7.95) + ΔH_{rxn} (13.65) kcal mol^{-1}.

k_{-6} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 13.65 kcal mol^{-1}.

k_7 A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.5 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 6.52 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_9 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for $C_3H_6 + CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 27.22 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_{10} A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_{11} A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (7.98) + ΔH_{rxn} (5.76) kcal mol^{-1}.

k_{-11} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 5.76 kcal mol^{-1}.

k_{12} A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.0 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_{13} A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_{14} A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.16 \times 10^{11}$ Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 14.45 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_{15} A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of four rotors (-4.3 × 4 cal mol^{-1} K^{-1}) and an optical isomer (OI) but gain an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (9.9) + ΔH_{rxn} (0.0) kcal mol^{-1}.

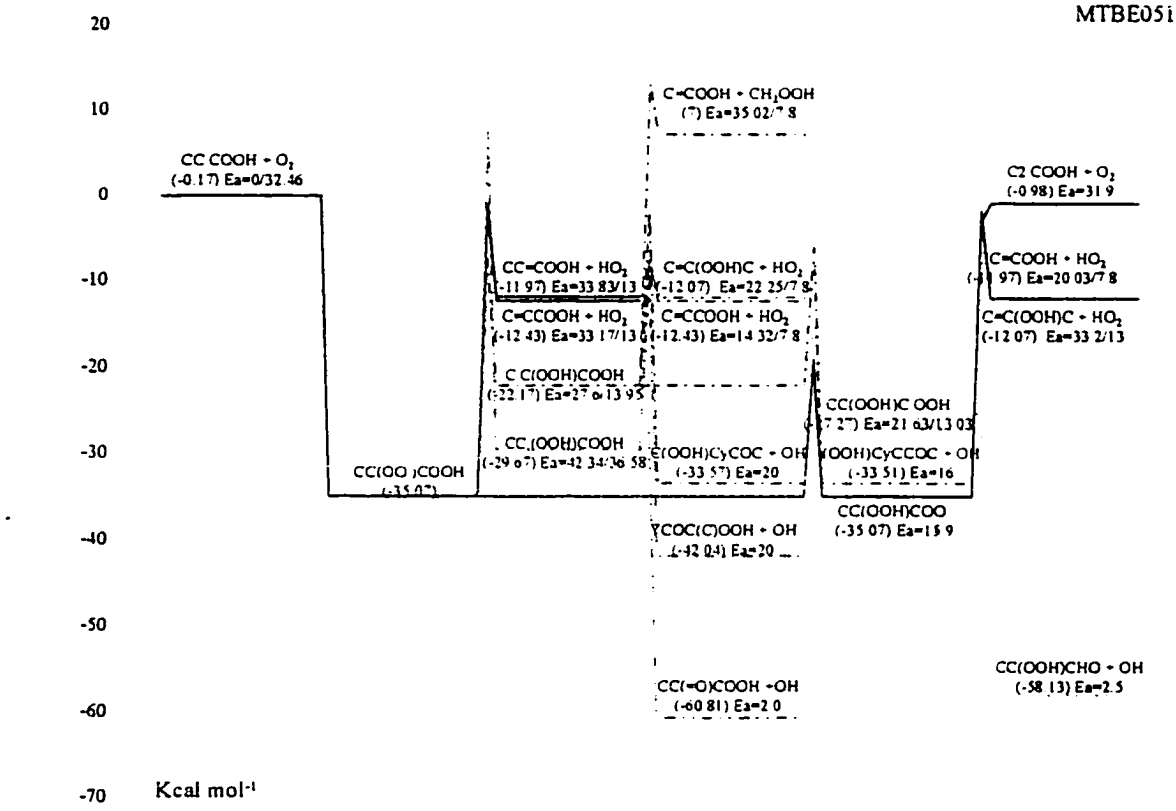
k_{-15} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 0.0 kcal mol^{-1}.

k_{16} A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.31 \times 10^{12}$ = 1/2 (CC.C + O_2), 92 ATK/BAU. $E_{a,f} = \Delta U_{rxn}$, = 32.46 kcal mol^{-1}.

k_{17} A_f is referenced from reaction C2COO. → CC=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (20.17) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_{18} A_f is referenced from reaction C2COO. → CC=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (20.83) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

IID. 73 CC.COOH + O_2 → Products



	Reaction	A $T^n e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC.COOH + O_2 → CC(OO.)COOH	3.31×10^{12} T^0 e^{-0T}	0.00
k_{-1}	CC(OO.)COOH → CC.COOH + O_2	4.90×10^{14} T^0 e^{-0T}	32.46
k_2	CC(OO.)COOH → C=CCOOH + HO_2	2.49×10^{9} $T^{1.18}$ e^{-0T}	33.17
k_3	CC(OO.)COOH → CC=COOH + HO_2	1.66×10^{9} $T^{1.18}$ e^{-0T}	33.83
k_4	CC(OO.)COOH → CC(OOH)C.OOH	2.99×10^{9} $T^{1.0}$ e^{-0T}	21.63
k_{-4}	CC(OOH)C.OOH → CC(OO.)COOH	7.82×10^{11} $T^{-0.33}$ $e^{-0.00073T}$	13.03
k_5	CC(OOH)C.OOH → CC(OOH)CHO + OH	3.21×10^{13} T^0 e^{-0T}	2.50
k_6	CC(OOH)C.OOH → CC=COOH + HO_2	1.48×10^{12} T^0 e^{-0T}	20.03
k_7	CC(OO.)COOH → C.C(OOH)COOH	4.49×10^{9} $T^{1.0}$ e^{-0T}	27.60
k_{-7}	C.C(OOH)COOH → CC(OO.)COOH	2.12×10^{11} $T^{-0.12}$ $e^{-0.00054T}$	13.95
k_8	C.C(OOH)COOH → CyCOC(COOH) + OH	4.68×10^{11} T^0 e^{-0T}	20.00
k_9	C.C(OOH)COOH → C=CCOOH + HO_2	4.82×10^{12} T^0 e^{-0T}	14.32
k_{10}	C.C(OOH)COOH → C=COOH + CH_2OOH	4.93×10^{12} T^0 e^{-0T}	35.02
k_{11}	C.C(OOH)COOH → CyCCOC(OOH) + OH	5.38×10^{10} T^0 e^{-0T}	16.00
k_{12}	CC(OO.)COOH → CC.(OOH)COOH	1.30×10^{10} $T^{1.0}$ e^{-0T}	42.34

	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_{-12}	CC.(OOH)COOH → CC(OO.)COOH	1.28×10^{11} $T^{0.04}$ $e^{-0.00072T}$	36.58
k_{13}	CC.(OOH)COOH → CC(=O)COOH + OH	8.71×10^{12} T^0 e^{-0T}	2.00
k_{14}	CC.(OOH)COOH → CyCOC(C)OOH + OH	4.68×10^{11} T^0 e^{-0T}	20.00
k_{15}	CC.(OOH)COOH → C=C(OOH)C + HO_2	2.94×10^{12} T^0 e^{-0T}	22.25
k_{16}	CC(OO.)COOH → CC(OOH)COO.	9.85×10^{6} $T^{1.0}$ e^{-0T}	15.90
k_{-16}	CC(OOH)COO. → CC(OO.)COOH	9.85×10^{6} $T^{1.0}$ e^{-0T}	15.90
k_{17}	CC(OOH)COO. → C2.COOH + O_2	1.04×10^{14} T^0 e^{-0T}	31.90
k_{18}	CC(OOH)COO. → C=C(OOH)C + HO_2	7.48×10^{9} $T^{0.73}$ e^{-0T}	33.20

frequency/degeneracy (CPFIT)
CC(OO.)COOH: 100.1 (10.107); 1059.7 (15.280); 2808.7 (8.113)
CC(OOH)C.OOH: 100.1 (11.462); 1084.1 (14.972); 2766.1 (6.566)
C.C(OOH)COOH: 100.0 (10.777); 1065.9 (15.825); 2784.7 (6.397)
CC.(OOH)COOH: 100.2 (11.914); 1126.4 (13.906); 2772.2 (7.180)
CC(OOH)COO.: 100.1 (10.107); 1059.7 (15.280); 2808.7 (8.113)
Lennard-Jones parameter
σ(Å) = 5.86, ε/k (K) = 632.06

k_1 1/2 (CC.C + O_2), 92 ATK/BAU.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -32.46 kcal mol^{-1}.

k_2 A_f is referenced from reaction C2COO. → CC=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (20.83) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_3 A_f is referenced from reaction C2COO. → CC=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (20.17) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_4 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (7.03) + ΔH_{rxn} (8.60) kcal mol^{-1}.

k_{-4} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 8.60 kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75\times10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.5\times10^{11}$ = 1/2(C=C + HO_2), 72 KER/PAR. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 12.23 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_7 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 3, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 2 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (7.95) + ΔH_{rxn} (13.65) kcal mol^{-1}.

k_{-7} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 13.65 kcal mol^{-1}.

k_8 A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_bT/h = $10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_9 MR 3.5×10^{11}, Bozzelli). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 6.52 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_{10} A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 27.22 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_{11} A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_bT/h = $10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_{12} A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI). $E_{a,f}$ = RS (26) + E_{abst} (7.98) + ΔH_{rxn} (5.76) kcal mol^{-1}.

k_{-12} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 5.76 kcal mol^{-1}.

k_{13} A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.0 kcal mol^{-1} as $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O$ + OH (1990 Page)

k_{14} A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_bT/h = $10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_{15} A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.16 \times 10^{11}$ Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 14.45 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

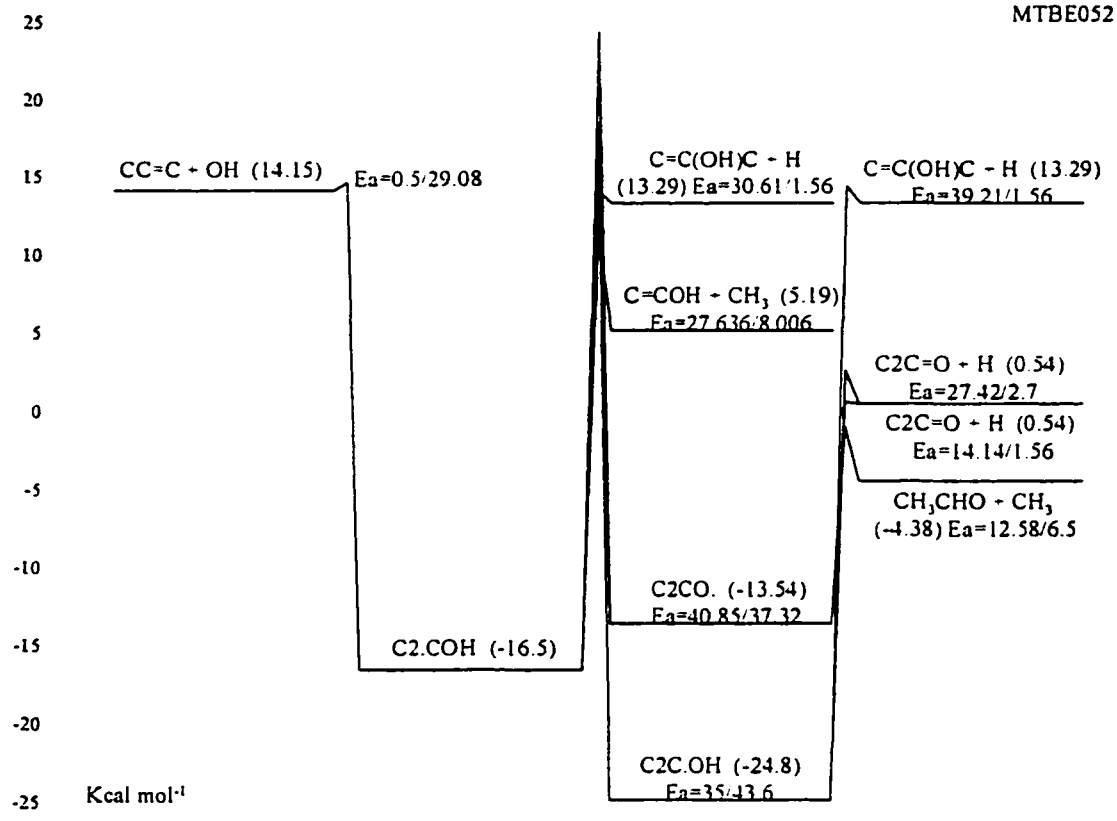
k_{16} A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (0).

k_{-16} A_r estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of four rotor (-4.3 × 4 cal mol^{-1} K^{-1}) and loss of one optical isomer but gain an new optical isomer (OI). $E_{a,f}$ = RS (6) + E_{abst} (9.90) + ΔH_{rxn} (0.00) kcal mol^{-1}.

k_{17} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{12}$, 88 XI for C3CC. + O_2. $E_{a,f} = \Delta U_{rxn}$, = 31.90 kcal mol^{-1}..

k_{18} A_f is referenced from reaction C2CCOO. $\rightarrow$ C2C=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (20.2) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

IID. 74 CC=C + OH → [C2.COH]* → Products



	Reaction	A $T^n e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC=C + OH → C2.COH	1.81×10^{13} T^0 e^{-0T}	0.50
k_{-1}	C2.COH → CC=C + OH	1.04×10^{14} T^0 e^{-0T}	29.08
k_2	C2.COH → C=COH + CH_3	7.11×10^{11} T^0 e^{-0T}	27.64
k_3	C2.COH → C=C(OH)C + H	1.86×10^{12} T^0 e^{-0T}	30.61
k_4	C2.COH → C2CO.	1.03×10^{9} $T^{1.01}$ $e^{-0.0005T}$	40.85
k_{-4}	C2CO. → C2.COH	3.90×10^{10} $T^{1.0}$ e^{-0T}	37.32
k_5	C2CO. → CH_3CHO + CH_3	7.44×10^{13} T^0 e^{-0T}	12.58
k_6	C2CO. → C2C=O + H	9.02×10^{12} T^0 e^{-0T}	14.14
k_7	C2.COH → C2C.OH	6.50×10^{9} $T^{1.0}$ e^{-0T}	35.00
k_{-7}	C2C.OH → C2.COH	9.09×10^{8} $T^{1.42}$ $e^{0.00017T}$	43.60
k_8	C2C.OH → C=C(OH)C + H	6.77×10^{12} T^0 e^{-0T}	39.21
k_9	C2C.OH → C2C=O + H	1.77×10^{12} T^0 e^{-0T}	27.42

frequency/degeneracy (CPFIT)
C2.COH: 250.9 (5.095); 1053.9 (11.950); 2837.8 (8.455)

C2CO.: 250.2 (4.688); 1065.6 (13.397); 2814.4 (7.915)
C2C.OH: 250.2 (5.519); 1129.1 (11.377); 2824.2 (8.604)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f is referenced from 89 ATK/BAU, E_a is estimated by Bozzelli.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -28.18 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 19.63 kcal mol^{-1}. $E_{a,r}$ = 8.006 kcal mol^{-1}. (referenced as the same as the A_r).

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12}$ = 1/2 (H + CC=C $\rightarrow$ CC.C, 91 TSA/HAM). $E_{a,f}$ is estimated by Bozzelli.

k_4 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (3.53) kcal mol^{-1}.

k_{-4} A_r estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}(T)/R$), deg. = 6, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain of an optical isomer (OI), $E_{a,r}$ = RS (26) + E_{abst} (11.32) kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.16 \times 10^{11}$ Bozzelli. $E_{a,f} = E_{a,r}$ + ΔU_{rxn}, ΔU_{rxn} = 6.08 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (estimated by Bozzelli).

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12}$ = 1/2 (H + CC=C $\rightarrow$ CC.C, 91 TSA/HAM). $E_{a,f}$ is taken from the same reference as A_r.

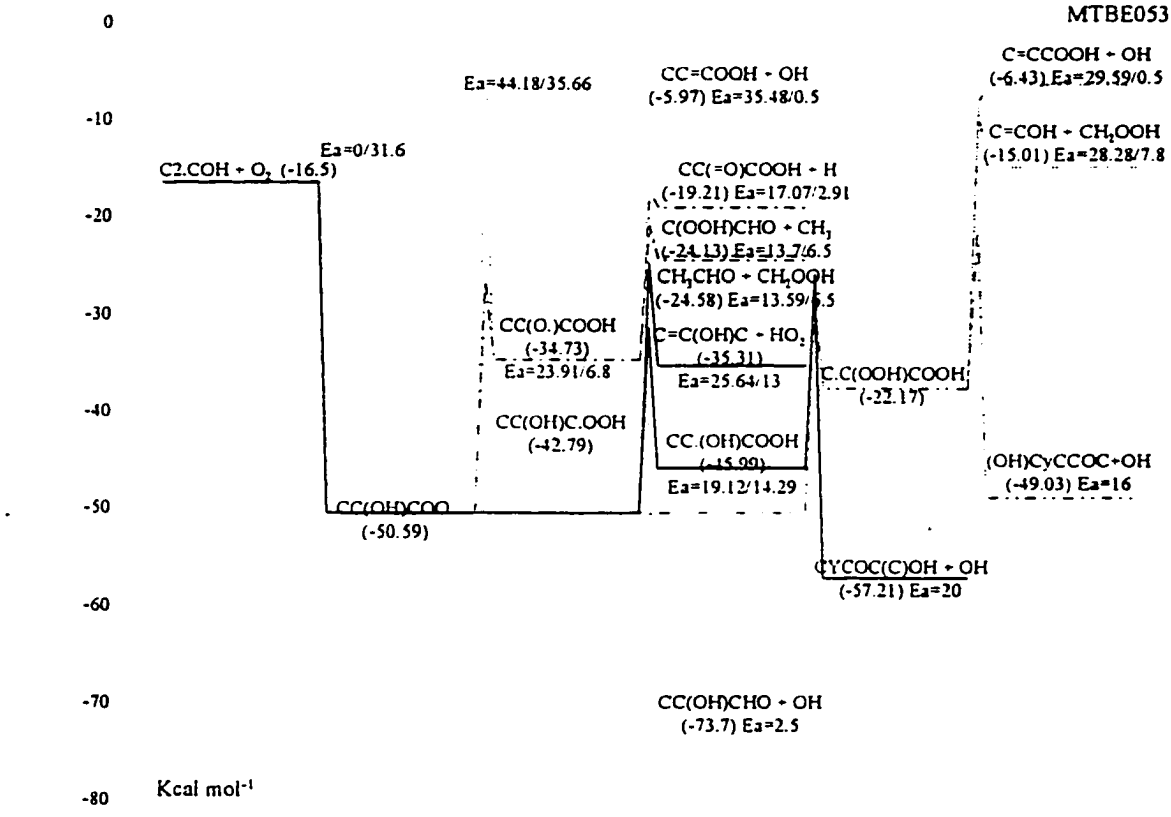
k_7 A_f estimated using TST, A = (deg.) (ek_b/h) T^n exp($\Delta S^{\neq}(T)/R$), deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}), $E_{a,r}$ = RS (28) + E_{abst} (7.0) kcal mol^{-1}.

k_{-7} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -8.6 kcal mol^{-1}.

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.30 \times 10^{13}$, 91 TSA/HAM for H + CC=C $\rightarrow$ CC.C, $E_{a,f}$ is estimated by Bozzelli.

k_9 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.30 \times 10^{13}$, 91 TSA/HAM for H + CC=C $\rightarrow$ CC.C, $E_{a,f}$ is taken from the same reference as A_r.

IID. 75 C2.COH + O_2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C2.COH + O_2 → CC(OH)COO.	1.00×10^{12} T^0 e^{-0T}	0.00
k_{-1}	CC(OH)COO. → C2.COH + O_2	1.08×10^{14} T^0 e^{-0T}	31.60
k_2	CC(OH)COO. → C=C(OH)C + HO_2	7.48×10^{9} $T^{0.74}$ e^{-0T}	25.64
k_3	CC(OH)COO. → CC(OH)C.OOH	2.60×10^{10} $T^{1.0}$ e^{-0T}	44.18
k_{-3}	CC(OH)C.OOH → CC(OH)COO.	4.38×10^{12} $T^{-0.26}$ $e^{-0.00072T}$	35.66
k_4	CC(OH)C.OOH → CC(OH)CHO + OH	1.24×10^{13} T^0 e^{-0T}	2.50
k_5	CC(OH)C.OOH → CC=COOH + OH	1.76×10^{13} T^0 e^{-0T}	35.48
k_6	CC(OH)COO. → C.C(OH)COOH	5.15×10^{8} $T^{1.0}$ e^{-0T}	21.67
k_{-6}	C.C(OH)COOH → CC(OH)COO.	1.41×10^{10} $T^{-0.03}$ $e^{-0.00037T}$	7.92
k_7	C.C(OOH)COOH → C=CCOOH + OH	6.58×10^{13} T^0 e^{-0T}	29.59
k_8	C.C(OOH)COOH → CyCCOC (OH) + OH	5.38×10^{10} T^0 e^{-0T}	16.00
k_9	C.C(OOH)COOH → C=COH + CH_2OOH	1.98×10^{12} T^0 e^{-0T}	28.28
k_{10}	CC(OH)COO. → CC.(OH)COOH	1.50×10^{9} $T^{1.0}$ e^{-0T}	19.12
k_{-10}	CC.(OH)COOH → CC(OH)COO.	3.55×10^{9} $T^{0.45}$ $e^{-0.0004T}$	14.29
k_{11}	CC.(OH)COOH → CyCOC(C)OH	4.68×10^{11} T^0 e^{-0T}	20.00

	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_{12}	CC(OH)COO. → CC(O.)COOH	1.72×10^{8} $T^{1.0}$ e^{-0T}	23.91
k_{-12}	CC(O.)COOH → CC(OH)COO.	1.67×10^{11} $T^{-0.05}$ $e^{-0.00002T}$	6.80
k_{13}	CC(O.)COOH → CH3CHO + CH_2OOH	2.24×10^{14} T^{0} e^{-0T}	13.59
k_{14}	CC(O.)COOH → C(OOH)CHO + CH_3	5.48×10^{13} T^{0} e^{-0T}	13.70
k_{15}	CC(O.)COOH → CC(=O)COOH + H	1.04×10^{13} T^{0} e^{-0T}	17.07

frequency/degeneracy (CPFIT)
CC(OH)COO.: 250.8 (9.217); 1122.7 (13.406); 2922.8 (8.377)
CC(OH)C.OOH: 100.2 (8.968); 1063.5 (14.069); 2832.3 (7.463)
C.C(OH)COOH: 250.2 (10.056); 1150.8 (13.940); 2841.4 (6.504)
CC.(OH)COOH: 100.9 (8.688); 1083.8 (13.748); 2790.4 (8.064)
CC(O.)COOH: 251.0 (9.668); 1140.1 (15.036); 2871.3 (6.296)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 taken from 88 XI for C3CC. + O_2 → C3CCOO.).

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -31.60 kcal mol^{-1}.

k_2 A_f is referenced from reaction C2CCOO. → C2C=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (12.64) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_3 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI), $E_{a,r}$ = RS (26) + E_{abst} (9.66) + ΔH_{rxn} (8.52) kcal mol^{-1}.

k_{-3} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -8.52 kcal mol^{-1}.

k_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75\times10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.5 kcal mol^{-1} based on $E_{a,f}$ for CH_2OOH → CH_2O + OH (1990 Page)

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.05\times10^{12}$ = 1/2 (OH + CC=C → C2.COH), 89 ATK/BAU. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (34.98) kcal mol^{-1}. $E_{a,r}$ = 0.5 kcal mol^{-1}. (estimated by Bozzelli).

k_6 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 3, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI), $E_{a,r}$ = RS (0) + E_{abst} (7.92) + ΔH_{rxn} (13.75) kcal mol^{-1}.

k_{-6} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 13.75 kcal mol^{-1}.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81\times10^{13}$, 89 ATK/BAU for

OH + C=C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (29.09) kcal mol^{-1}. $E_{a,r}$ = 0.5 kcal mol^{-1}. (estimated by Bozzelli).

k_8 A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_9 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + $CH_3 \rightarrow$ C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (21.26) kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_{10} A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}) and gain an optical isomer (OI), $E_{a,r}$ = RS (6) + E_{abst} (8.29) + ΔH_{rxn} (4.83) kcal mol^{-1}.

k_{-10} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 4.83 kcal mol^{-1}.

k_{11} A_f estimated using TST, A = (deg.) (ek_bT/h) $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_bT/h = 10^{13.55}$? , $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}). $E_{a,f}$ is evaluated in this study.

k_{12} A_f estimated using TST, A = (deg.) (ek_b/h) $T^n \exp(\Delta S^{\neq}(T)/R)$, deg. = 1, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3 × 2 cal mol^{-1} K^{-1}) and gain an optical isomer (OI), $E_{a,r}$ = RS (0) + E_{abst} (6.80) + ΔH_{rxn} (17.11) kcal mol^{-1}.

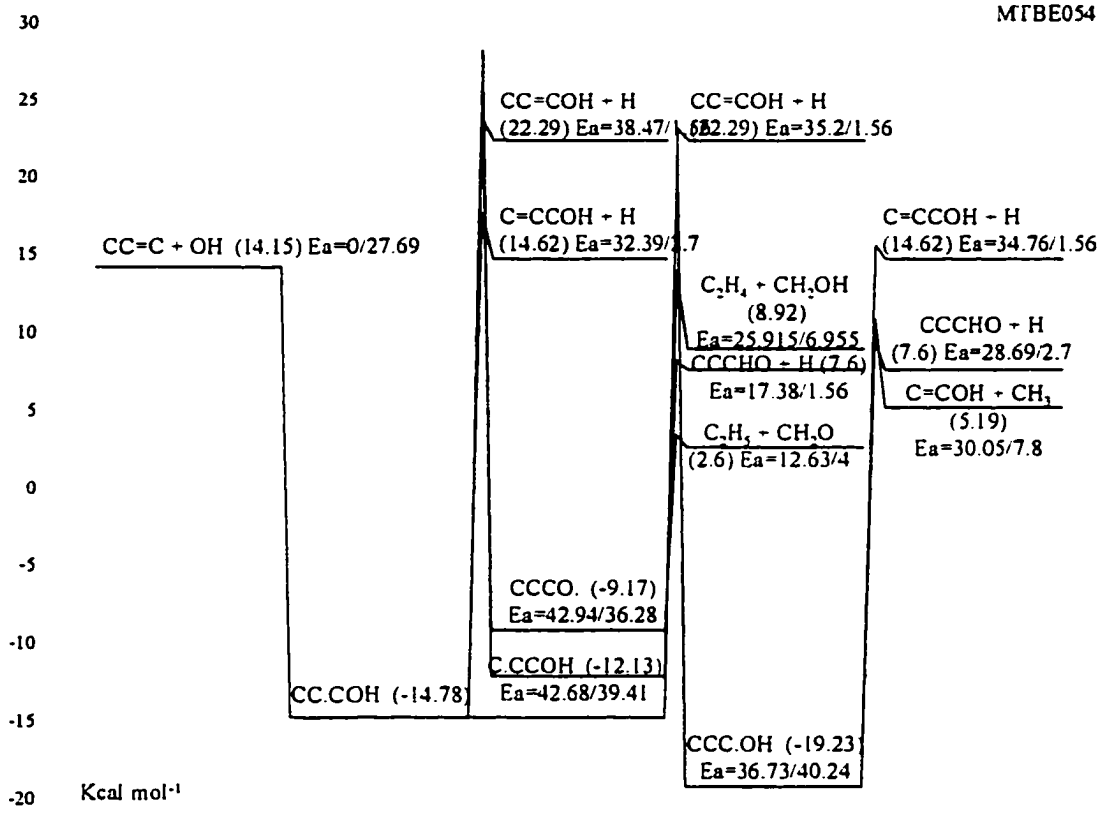
k_{-12} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 17.11 kcal mol^{-1}.

k_{13} A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.16 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 7.09 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (estimated by Bozzelli).

k_{14} A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.16 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 7.20 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (estimated by Bozzelli).

k_{15} A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.62 \times 10^{12}$ = 1/2 (H + CC=C $\rightarrow$ CCC., 91 TSA/HAM). $E_{a,f}$ is estimated by Bozzelli.

IID. 76 CC=C + OH → [CC.COH]* → Products



	Reaction	A $T^n e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC=C + OH → CC.COH	1.81×10^{13} T^0 e^{-0T}	0.00
k_{-1}	CC.COH → CC=C + OH	7.59×10^{13} T^0 e^{-0T}	27.69
k_2	CC.COH → C=CCOH + H	5.83×10^{12} T^0 e^{-0T}	38.47
k_3	CC.COH → CC=COH + H	1.56×10^{12} T^0 e^{-0T}	32.39
k_4	CC.COH → CCCO.	3.16×10^{10} $T^{1.86}$ $e^{-0.00002T}$	42.94
k_{-4}	CCCO. → CC.COH	1.30×10^{10} $T^{1.0}$ e^{-0T}	36.28
k_5	CCCO. → CH_2O + C_2H_5	2.30×10^{13} T^0 e^{-0T}	12.63
k_6	CCCO. → CCCHO + H	2.04×10^{13} T^0 e^{-0T}	17.38
k_7	CC.COH → CCC.OH	1.30×10^{10} $T^{1.0}$ e^{-0T}	36.73
k_{-7}	CCC.OH → CC.COH	4.60×10^{14} $T^{-0.49}$ $e^{0.00075T}$	40.24
k_8	CCC.OH → C=COH + CH_3	3.90×10^{12} T^0 e^{-0T}	30.05
k_9	CCC.OH → CCCHO + H	1.26×10^{13} T^0 e^{-0T}	28.69
k_{10}	CCC.OH → CC=COH + H	4.00×10^{12} T^0 e^{-0T}	34.76
k_{11}	CC.COH → C.CCOH	1.95×10^{10} $T^{1.0}$ e^{-0T}	42.68
k_{-11}	C.CCOH → CC.COH	2.31×10^{10} $T^{0.11}$ $e^{-0.0004T}$	39.41

	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_{12}	$C.CCOH \rightarrow C_2H_4 + CH_2OH$	9.47×10^{11} T^0 e^{-0T}	25.92
k_{13}	$C.CCOH \rightarrow C{=}CCOH + H$	2.18×10^{12} T^0 e^{-0T}	35.20

frequency/degeneracy (CPFIT)
CC.COH: 410.4 (7.198); 1475.4 (12.281); 3204.6 (6.022)
CCCO.: 494.7 (8.503); 1392.3 (11.260); 3093.2 (6.238)
CCC.OH: 469.0 (9.204); 1376.7 (9.627); 3068.0 (6.668)
C.CCOH: 475.9 (8.453); 1397.0 (10.702); 3138.2 (6.345)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f is referenced from 89 ATK/BAU, E_a is estimated by Bozzelli.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -27.69 kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.30 \times 10^{13}$, 91 TSA/HAM for H + CC=C → CC.C, $E_{a,f}$ is taken from the same reference as A_f.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.62 \times 10^{12}$ = 1/2 (H + CC=C → CCC.), 91 TSA/HAM. $E_{a,f}$ is estimated by Bozzelli.

k_4 A_f via A_r and Microscopic Reversbility (MR), $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (6.66) kcal mol^{-1}.

k_{-4} A_r estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 6, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain of an optical isomer (OI), $E_{a,r}$ = RS (26) + E_{abst} (10.28) kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.58 \times 10^{11}$, 72 KER/PAR for CC. + C=C → CCCC.. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 8.63 kcal mol^{-1}. $E_{a,r}$ = 4.968 kcal mol^{-1}. (estimated by Bozzelli).

k_6 A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12}$ = 1/2 (H + CC=C → CC.C), 91 TSA/HAM. $E_{a,f}$ is taken from the same reference as A_r.

k_7 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 2, $ek_b/h = 5.66 \times 10^{10}$, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}), $E_{a,r}$ = RS (28) + E_{abst} (8.73) kcal mol^{-1}.

k_{-7} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -3.51 kcal mol^{-1}.

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.69 \times 10^{11}$, 91 TSA for CH_3 + CC=C → CC.CC. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 22.25 kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_9 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.30 \times 10^{13}$, 91 TSA/HAM for H + CC=C → CC.C, $E_{a,f}$ is estimated by Bozzelli.

k_{10} A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12}$ = 1/2 (H + CC=C → CC.C), 91 TSA/HAM. $E_{a,f}$ is taken from the same reference as A_r.

k_{11} A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 3, ek_b/h =

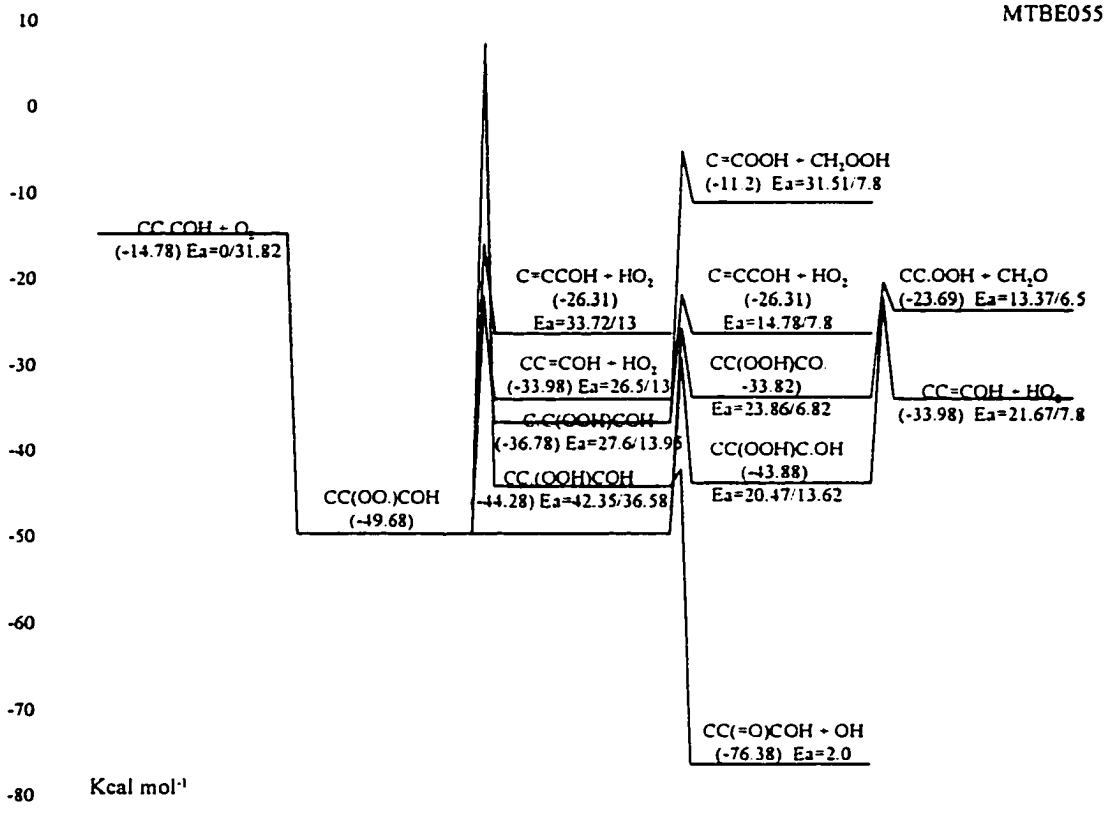
5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}), $E_{a,r}$ = RS (28) + E_{abst} (12.41) + ΔH_{rxn} (3.27) kcal mol^{-1}.

k_{11} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 3.27 kcal mol^{-1}.

k_{12} A_f via A_r and Microscopic Reversbility (MR), $A_r = 4.82 \times 10^{10}$, 87 TSA/HAM, $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (18.96) kcal mol^{-1}, $E_{a,r}$=6.955 kcal mol^{-1} from the same reference as A_r.

k_{13} A_f via A_r and Microscopic Reversbility (MR), $A_r = 6.50 \times 10^{12}$ = 1/2 (H + CC=C → CC.C), 91 TSA/HAM. $E_{a,f}$ is taken from the same reference as A_r.

IID. 77 CC.COH + O2 → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC.COH + O_2 → CC(OO.)C OH	3.31×10^{12} T^0 e^{-0T}	0.00
k_{-1}	CC(OO.)C OH → CC.COH + O_2	8.71×10^{14} T^0 e^{-0T}	31.82
k_2	CC(OO.)C OH → C=CCOH + HO_2	2.49×10^{9} $T^{1.18}$ e^{-0T}	33.72
k_3	CC(OO.)C OH → CC=COH + HO_2	1.66×10^{9} $T^{1.18}$ e^{-0T}	26.50
k_4	CC(OO.)COH → CC.(OOH)COH	1.30×10^{10} $T^{1.0}$ e^{-0T}	42.35
k_{-4}	CC.(OOH)COH → CC(OH)COO.	1.39×10^{11} $T^{0.03}$ $e^{-0.00072T}$	36.58
k_5	CC.(OOH)COH → CC=COOH + OH	4.50×10^{12} T^0 e^{-0T}	2.00
k_6	CC(OO.)COH → C.C(OOH)COH	4.49×10^{9} $T^{1.0}$ e^{-0T}	27.60
k_{-6}	C.C(OOH)COH → CC(OO.)C OH	2.20×10^{11} $T^{-0.12}$ $e^{-0.00055T}$	13.95
k_7	C.C(OOH)COH → C=CCOH + HO_2	3.33×10^{12} T^0 e^{-0T}	14.87
k_8	C.C(OOH)COH → C=COOH + CH_2OH	2.41×10^{12} T^0 e^{-0T}	31.51
k_9	CC(OO.)COH → CC(OOH)C.OH	2.99×10^{9} $T^{1.0}$ e^{-0T}	20.47
k_{-9}	CC(OOH)C.OH → CC(OO.)COH	2.52×10^{13} $T^{-0.68}$ $e^{-0.00087T}$	13.62
k_{10}	CC(OOH)C.OH → CC=COH + HO_2	1.50×10^{13} T^0 e^{-0T}	21.67
k_{11}	CC(OO.)COH → CC(OOH)CO.	1.72×10^{8} $T^{1.0}$ e^{-0T}	23.86

	Reaction	A $T^n e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_{11}	CC(OOH)CO. → CC(OO.)COH	1.72×10^{11} $T^{-0.06}$ $e^{-0.00009T}$	6.82
k_{12}	CC(OOH)CO. → CC.OOH + CH_2O	3.76×10^{13} T^{0} e^{-0T}	13.37

frequency/degeneracy (CPFIT)
CC(OO.)COH: 263.2 (9.166); 1129.6 (13.243); 2947.7 (8.591
CC.(OOH)COH: 250.0 (11.027); 1240.8 (12.207); 2978.8 (7.266)
C.C(OOH)COH: 292.6 (10.537); 1176.0 (13.350); 3006.3 (6.612)
CC(OOH)C.OH: 292.8 (11.036); 1145.0 (12.686); 2968.5 (6.777)
CC(OOH)CO.: 274.5 (9.794); 1144.0 (14.514); 2929.5 (6.692)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 A_f = 1/2 (CC.C + O_2), 92 ATK/BAU, $E_{a,f}$ is taken from the same reference.

k_{-1} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = \Delta U_{rxn}$ = 31.82 kcal mol^{-1}.

k_2 A_f is referenced from reaction C2COO. → CC=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (20.72) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_3 A_f is referenced from reaction C2COO. → CC=C + HO_2, (from thermal reaction analysis (AFACT2f) based on the thermodynamic properties calculated from MOPAC PM3 (corrected with internal rotor, electronic spin and optical isomer). $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (13.50) $E_{a,r}$ is estimated as ring strain (6) + $E_{a,add}$ (7).

k_4 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of one rotor (-4.3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI), $E_{a,r}$ = RS (26) + E_{abst} (10.58) + ΔH_{rxn} (5.77) kcal mol^{-1}.

k_{-4} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = -5.77 kcal mol^{-1}.

k_5 A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.75 \times 10^{12}$ = 1/2 (OH + C=C). $E_{a,f}$ estimated the same 2.0 kcal mol^{-1} based on $E_{a,f}$ for $CH_2OOH \rightarrow CH_2O + OH$ (1990 Page)

k_6 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 3, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3 × 3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI), $E_{a,r}$ = RS (6) + E_{abst} (7.95) + ΔH_{rxn} (13.65) kcal mol^{-1}.

k_{-6} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 13.65 kcal mol^{-1}.

k_7 A_f via A_r and Microscopic Reversbility (MR), $A_r = 3.50 \times 10^{11}$, Bozzelli. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 7.07 kcal mol^{-1}. $E_{a,r}$ = 7.80 kcal mol^{-1}. (estimated by Bozzelli).

k_8 A_f via A_r and Microscopic Reversbility (MR), $A_r = 9.64 \times 10^{10}$, 91 TSA for C_3H_6 + CH_3 → C3.C. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (23.71) kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated

by Bozzelli).

k_9 A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 2, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of two rotors (-4.3×2 cal mol^{-1} K^{-1}) and gain an optical isomer (OI), $E_{a,r}$ = RS (6) + E_{abst} (7.62) + ΔH_{rxn} (6.85) kcal mol^{-1}.

k_{-9} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 6.85 kcal mol^{-1}.

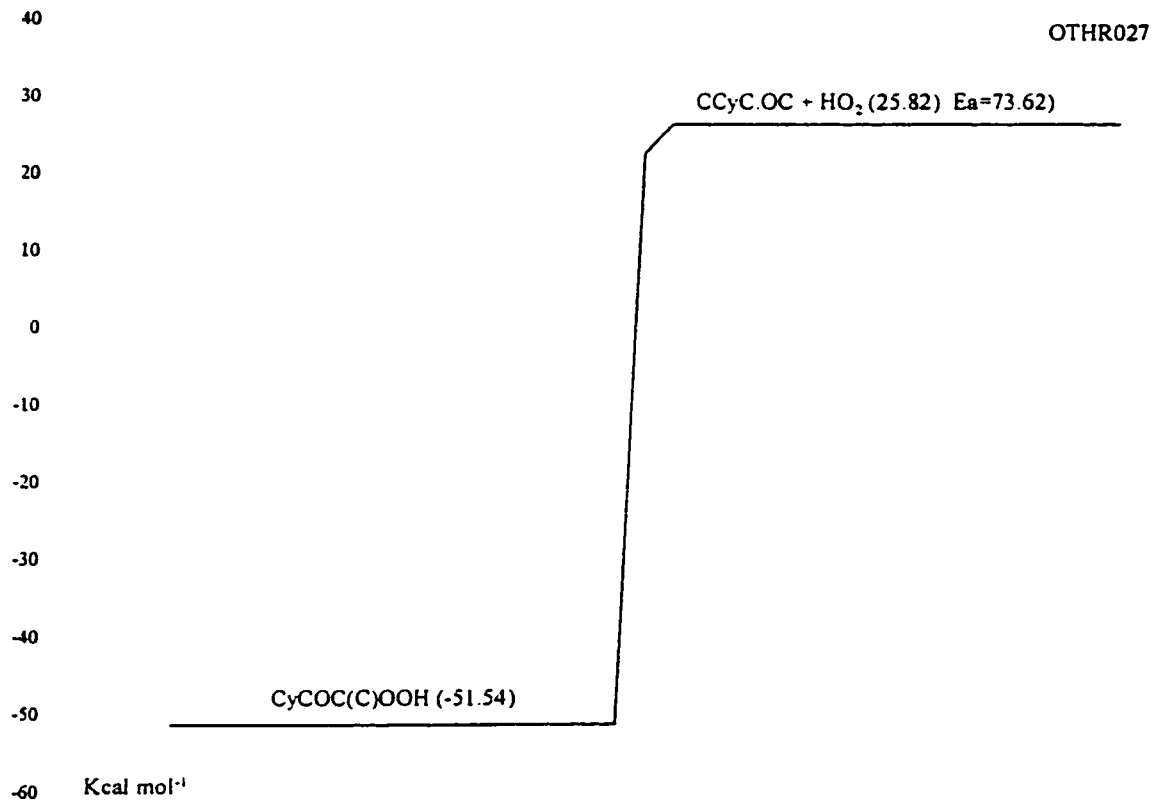
k_{10} A_f via A_r and Microscopic Reversbility (MR), $A_r = 2.50 \times 10^{11}$ = 1/2 (HO_2 + C=C), 72 KER/PAR. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (13.87) kcal mol^{-1}. $E_{a,r}$ = 7.8 kcal mol^{-1}. (estimated by Bozzelli).

k_{11} A_f estimated using TST, A = (deg.) (ek_b/h) T^n $\exp(\Delta S^{\neq}(T)/R)$, deg. = 1, ek_b/h = 5.66×10^{10}, n = 1.0, $\Delta S^{\neq}(T)$ is estimated as loss of three rotors (-4.3×3 cal mol^{-1} K^{-1}) and gain an optical isomer (OI), $E_{a,r}$ = RS (0) + E_{abst} (6.82) + ΔH_{rxn} (17.04) kcal mol^{-1}.

k_{-11} A_r via A_f and Microscopic Reversbility (MR), $E_{a,r} = E_{a,f} - \Delta U_{rxn}$, ΔU_{rxn} = 17.04 kcal mol^{-1}.

k_{12} A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.08 \times 10^{11}$, 88 TSA for CH_2O + CC.C $\rightarrow$ CCC + CHO. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$, ΔU_{rxn} = 8.2 kcal mol^{-1}. $E_{a,r}$ = 6.5 kcal mol^{-1}. (taken from the same reference).

IID. 78 CyCOC(C)OOH → CCyCOC. + HO_2

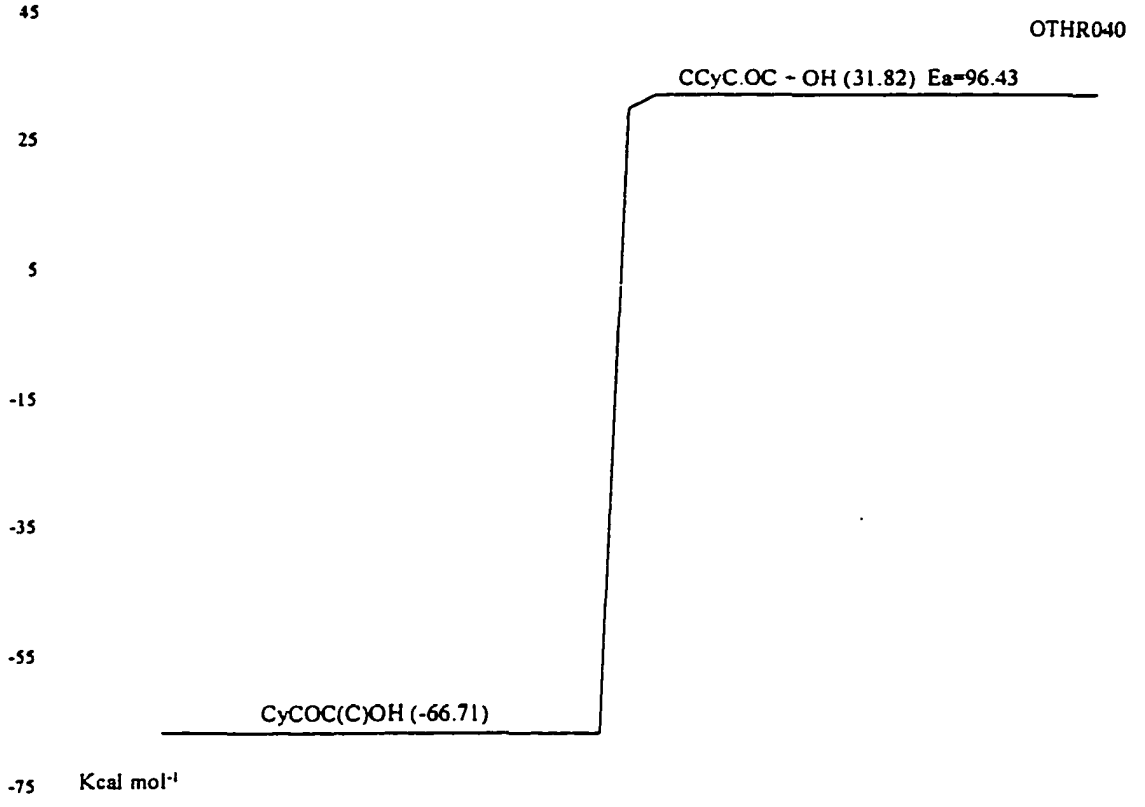


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CyCOC(C)OOH → CCyC.OC + HO_2	5.61×10^{16} T^0 e^{-0T}	73.62

frequency/degeneracy (CPFIT)
CyCOC(C)OOH: 250.2 (6.957); 976.8 (14.529); 2436.2 (7.015)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{13} = 1/2$ ($CH_3 + HO_2 \rightarrow CH_3O + OH$), 86 TSA/HAM, $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (73.62) kcal mol^{-1}.

IID. 79 CyCOC(C)OH → CCyC.OC + OH

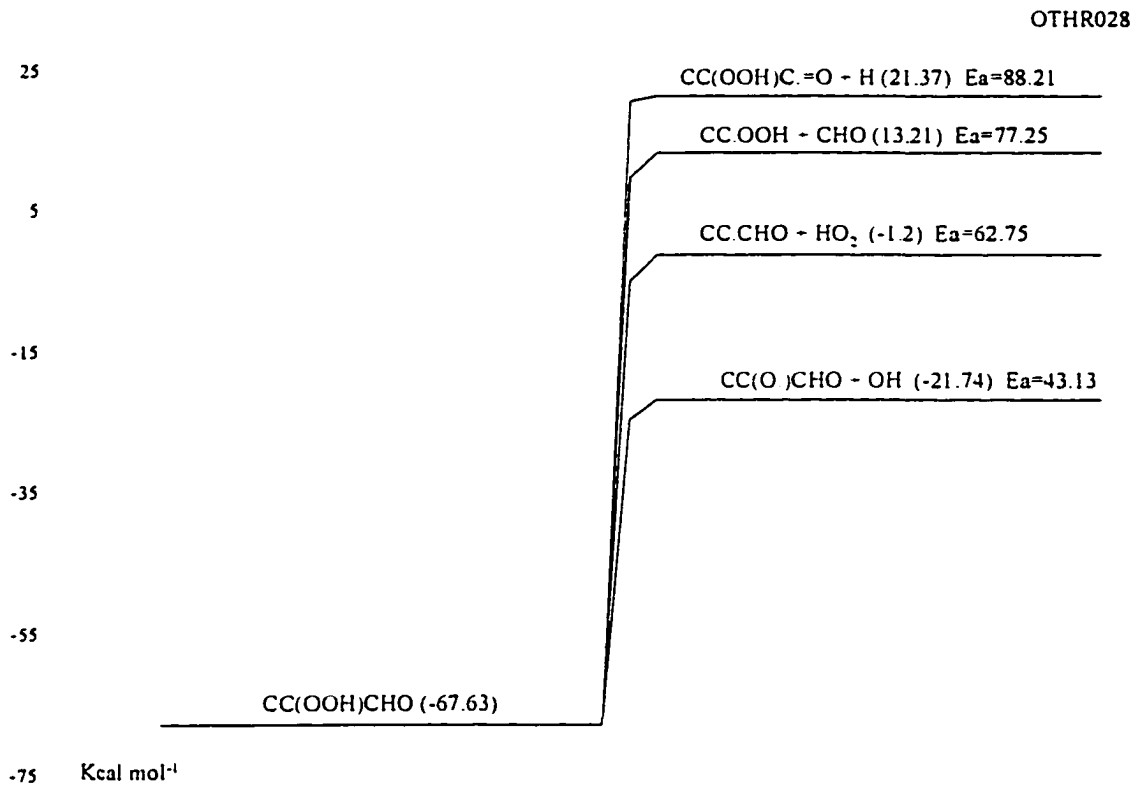


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CyCOC(C)OH → CCyC.OC + OH	6.18×10^{16} T^0 e^{-0T}	96.43

frequency/degeneracy (CPFIT)
CyCOC(C)OH: 489.2 (9.211); 1324.4 (11.691); 3257.3 (5.098)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, 90 TSA/HAM for C3C. + OH. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (96.43) kcal mol^{-1}.

IID. 80 CC(OOH)CHO → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC(OOH)CHO → CC.OOH + CHO	3.44×10^{16} T^0 e^{-0T}	77.25
k_2	CC(OOH)CHO → CC.CHO + HO_2	5.11×10^{14} T^0 e^{-0T}	62.75
k_3	CC(OOH)CHO → CC(OOH)C.=O + H	9.78×10^{14} T^0 e^{-0T}	88.21
k_4	CC(OOH)CHO → CC(O.)CHO + OH	6.57×10^{14} T^0 e^{-0T}	43.13

frequency/degeneracy (CPFIT)
CC(OOH)CHO: 250.2 (7.103); 924.9 (13.196); 2314.3 (7.701)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

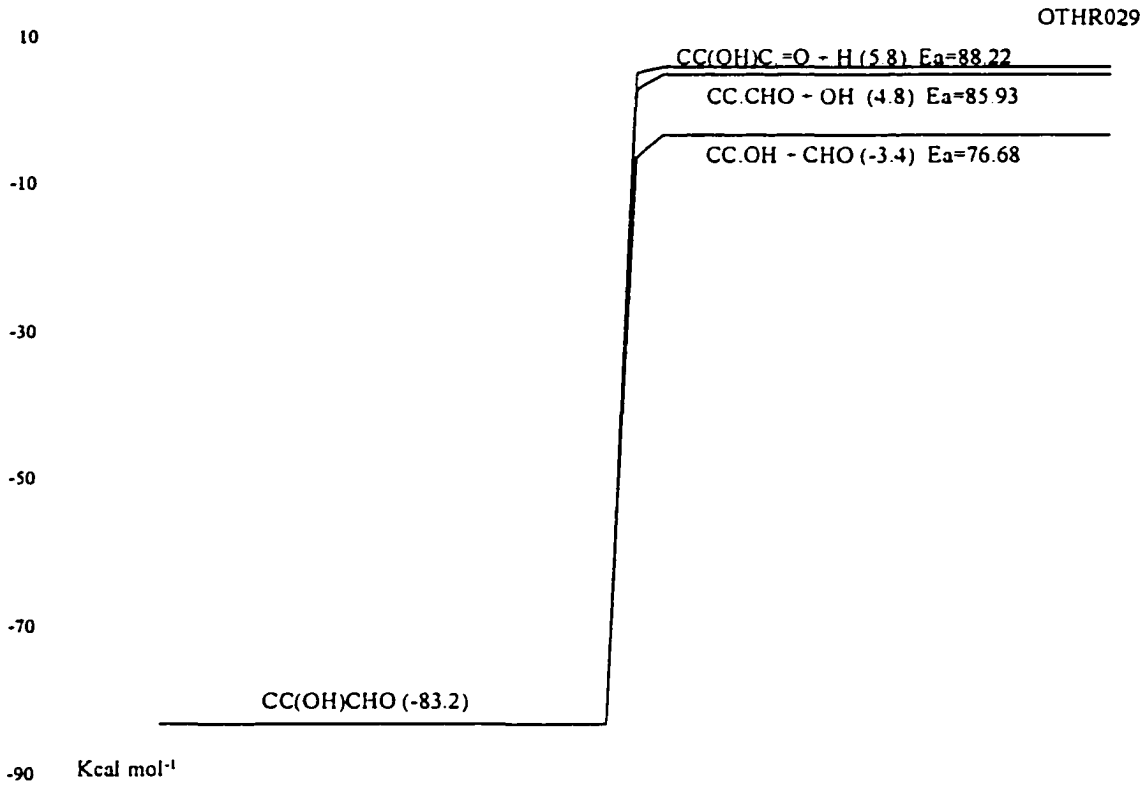
k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, 88 TSA/HAM for CC.C + CHO. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (77.25) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.00 \times 10^{13} = 1/2$ ($CH_3 + HO_2 \rightarrow CH_3O + OH$, 86 TSA/HAM). $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (62.75) kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{13}$ 1/2 (H + CHO), NIST FIT. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (88.21) kcal mol^{-1}.

K_4 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$ 92 BAU/COB for $CH_3O + O$. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (43.13) kcal mol^{-1}.

IID. 81 CC(OH)CHO → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC(OH)CHO → CC.OH + CHO	1.37×10^{16} T^0 e^{-0T}	76.68
k_2	CC(OH)CHO → CC.CHO + OH	6.61×10^{14} T^0 e^{-0T}	85.93
k_3	CC(OH)CHO → CC(OH)C.=O + H	4.95×10^{14} T^0 e^{-0T}	88.22

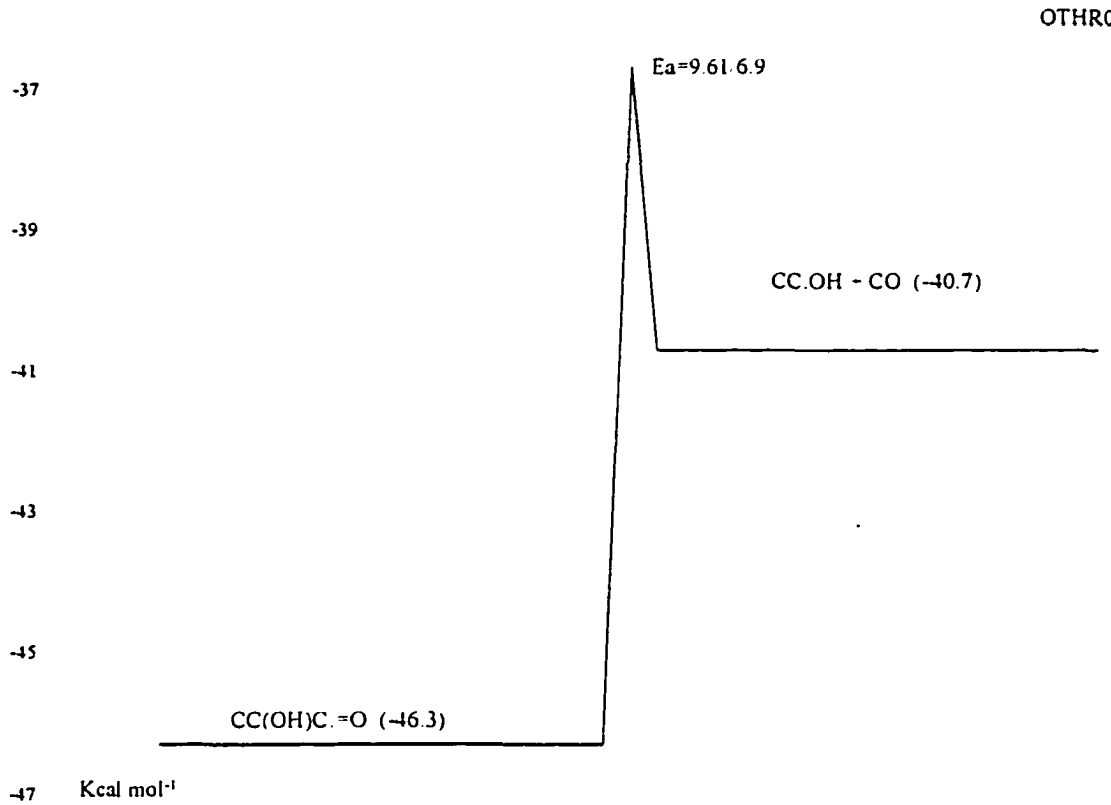
frequency/degeneracy (CPFIT)
CC(OH)CHO: 250.3 (5.563); 1060.1 (13.058); 2806.5 (6.878)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, 88 TSA/HAM for CC.C + CHO. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (76.68) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{13}$, 91 TSA/HAM for C=CC. + OH. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (85.93) kcal mol^{-1}.

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{13}$ 1/2 (H + CHO), NIST FIT. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (88.22) kcal mol^{-1}.

IID. 82 CC(OH)C.=O → CC.OH + CO

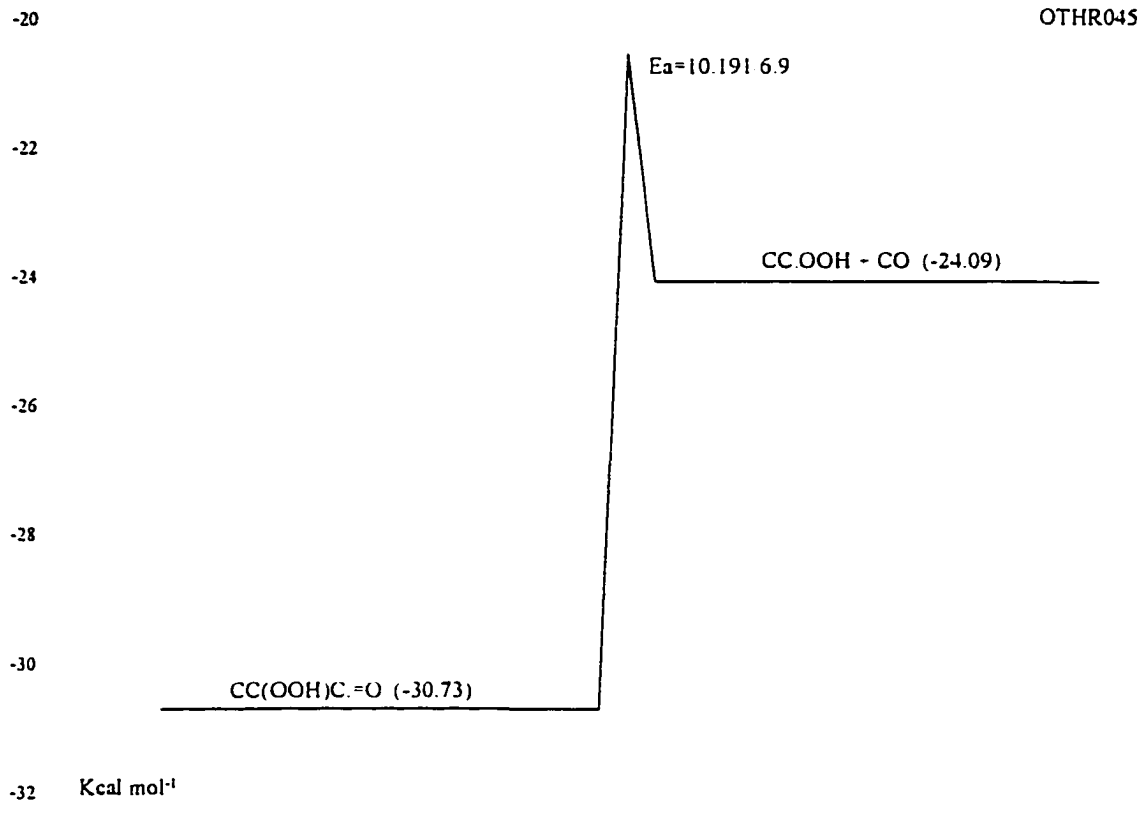


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC(OH)C.=O → CC.OH + CO	2.19×10^{12} T^0 e^{-0T}	9.61

frequency/degeneracy (CPFIT)
CC(OH)C.=O: 250.3 (5.384); 1058.9 (11.400); 2797.0 (5.716)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.01 \times 10^{10}$, 72 KER/PAR for CC.C + C_2H_2. $E_{a,f} = E_{a,f}$ (6.9) + ΔU_{rxn} (2.71) kcal mol^{-1}.

IID. 83 CC(OOH)C.=O → CC.OOH + CO

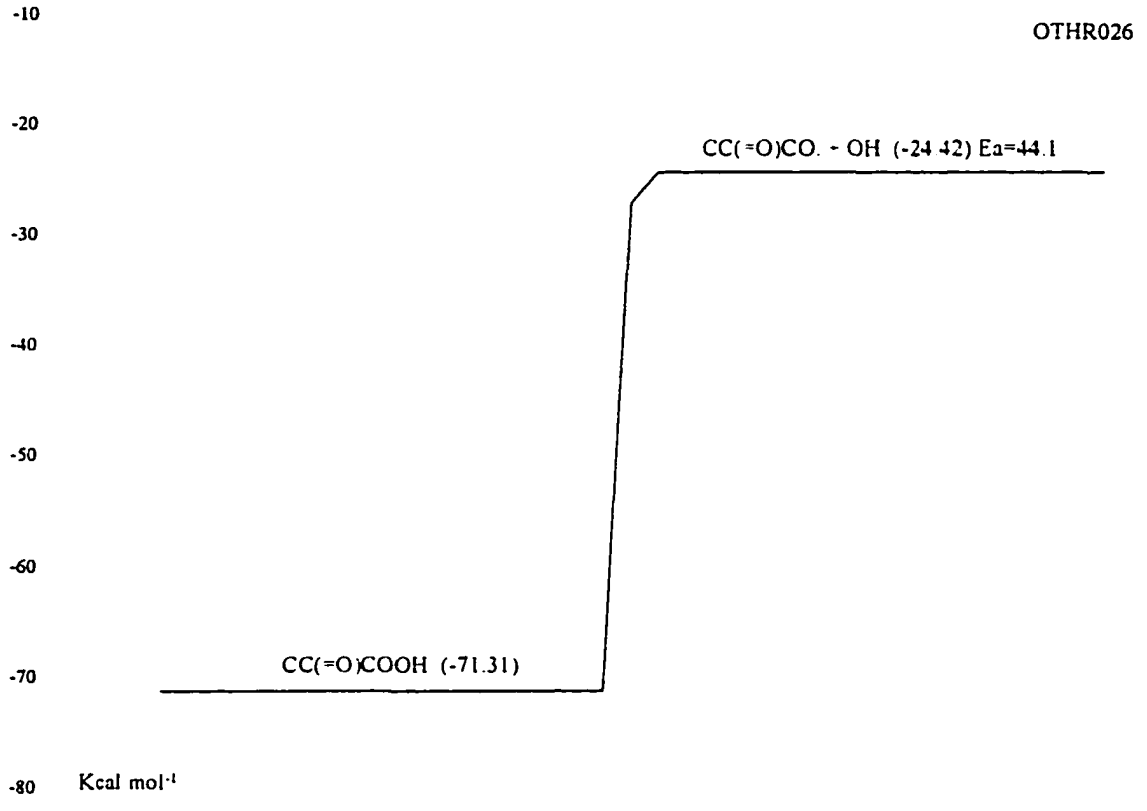


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC(OOH)C.=O → CC.OOH + CO	2.79×10^{12} T^0 e^{-0T}	10.19

frequency/degeneracy (CPFIT)
CC(OOH)C.=O: 250.8 (6.693); 887.0 (11.549); 2197.9 (6.758)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.01 \times 10^{10}$, 72 KER/PAR for CC.C + C_2H_2. $E_{a,f} = E_{a,f}$ (6.9) + ΔU_{rxn} (3.29) kcal mol^{-1}.

IID. 84 CC(=O)COOH → CC(=O)CO. + OH

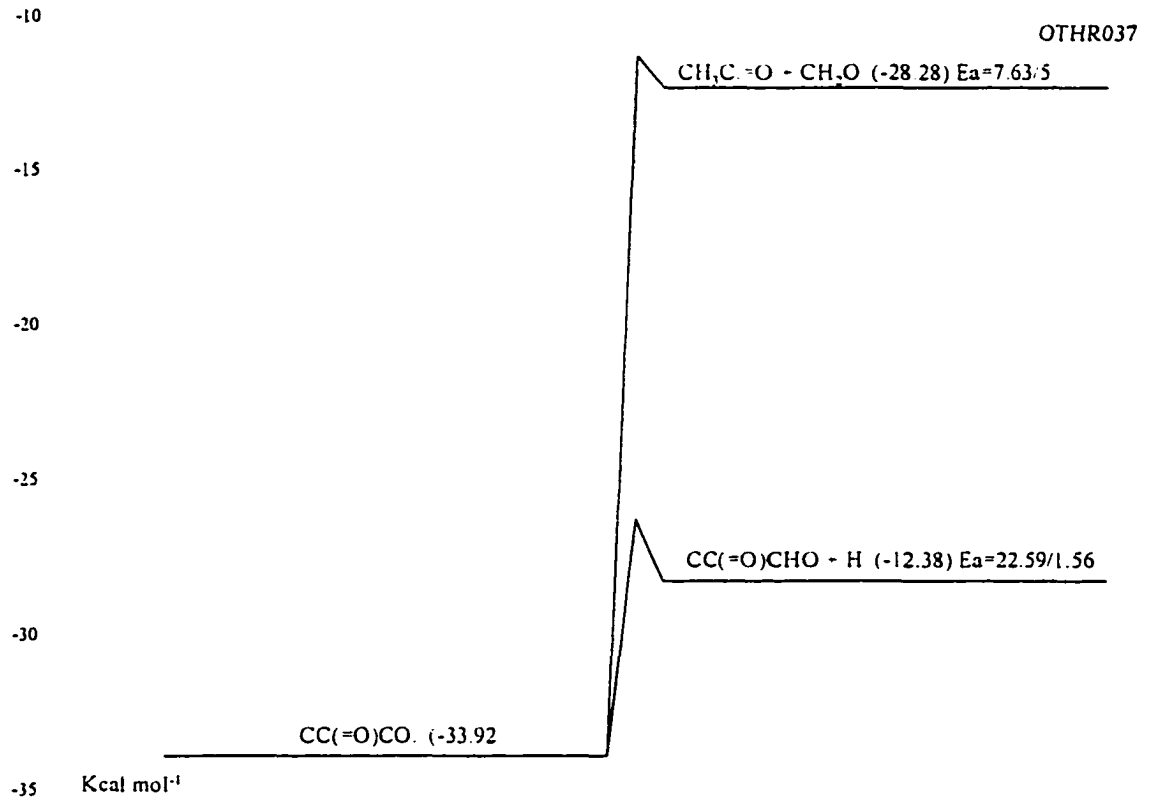


	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC(=O)COOH → CC(=O)CO. + OH	1.06×10^{15} T^0 e^{-0T}	44.10

frequency/degeneracy (CPFIT)
CC(=O)COOH: 325.0 (9.173); 877.0 (7.704); 2125.7 (11.123)
Lennard-Jones parameter
σ(Å) = 5.55, ε/k (K) = 584.86

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.81 \times 10^{13}$, 92 BAU/COB for CH_3O + OH. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (44.10) kcal mol^{-1}.

IID. 85 CC(=O)CO. → Products



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	CC(=O)CO. → CC(=O)CHO + H	7.28×10^{12} T^0 e^{-0T}	22.59
k_3	CC(=O)CO. → $CH_3C.=O$ + CH_2O	1.00×10^{13} T^0 e^{-0T}	7.63

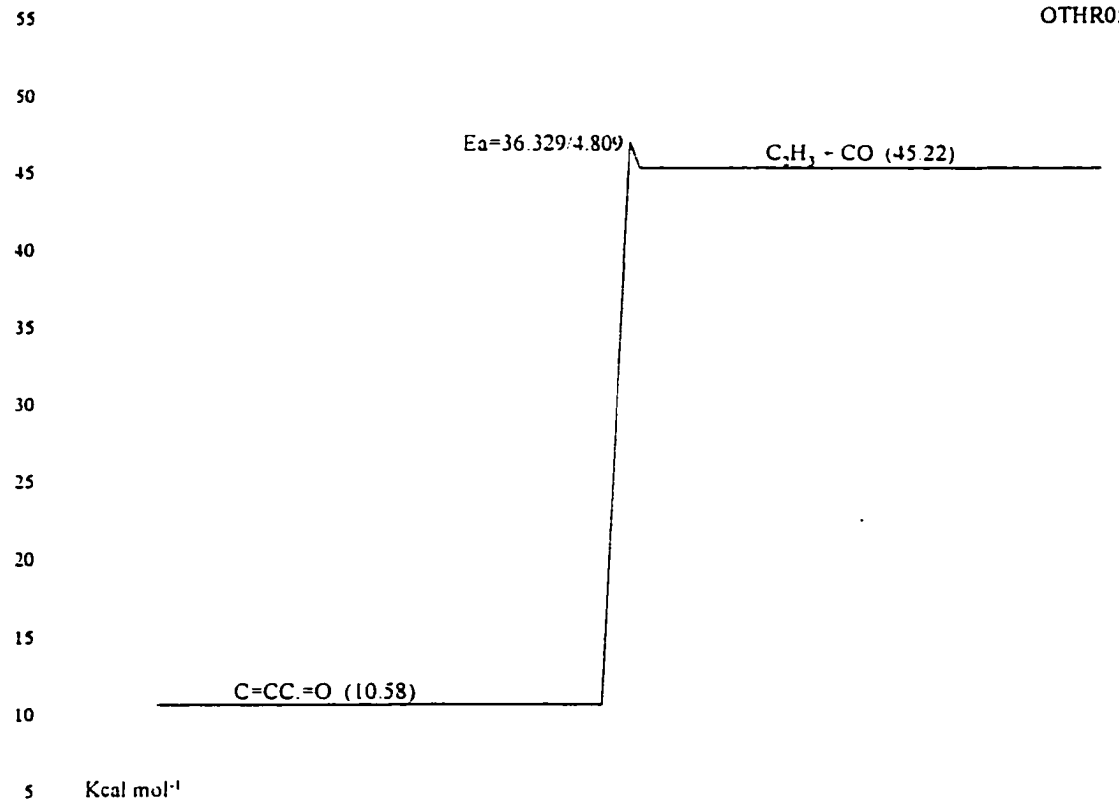
frequency/degeneracy (CPFIT)
CC(=O)CO.: 469.2 (9.796); 1694.2 (9.877); 3139.4 (3.327)
Lennard-Jones parameter
σ(Å) = 5.20, ε/k (K) = 533.08

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{12} = 1/2$ (H + C=C). $E_{a,f} = E_{a,r}$ (1.56) + ΔU_{rxn} (21.03) kcal mol^{-1}.

k_2 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.08 \times 10^{11}$, 88 TSA for CH_2O + CC.C → CCC + CHO. $E_{a,f} = E_{a,r} + \Delta U_{rxn}$ (2.63) kcal mol^{-1}. $E_{a,r} = 6.0$ kcal mol^{-1}. (estimated by Bozzelli).

k_3 A_f via A_r and Microscopic Reversbility (MR), $A_r = 5.00 \times 10^{13}$ 1/2 (H + CHO), NIST FIT. $E_{a,f} = E_{a,f}(0) + \Delta U_{rxn}$ (88.22) kcal mol^{-1}.

IID. 86 C=CC.=O → C2H3 + CO



	Reaction	A T^n $e^{-\alpha T}$ (s^{-1} or cm^3 mol^{-1} s^{-1})	E_a (kcal mol^{-1})
k_1	C=CC.=O → C_2H_3 + CO	3.13×10^{13} T^0 e^{-0T}	36.33

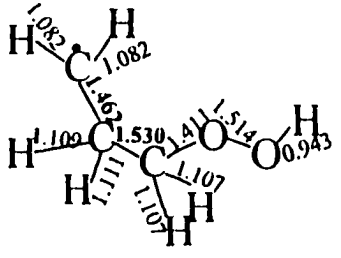
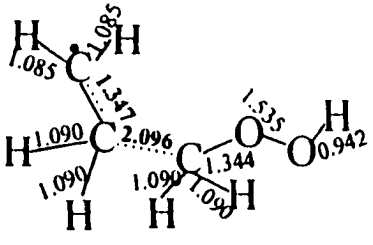
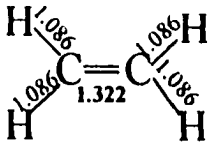
frequency/degeneracy (CPFIT)
C=CC.=O: 450.7 (5.070); 1031.9 (5.583); 2692.0 (3.848)
Lennard-Jones parameter
σ(Å) = 4.80, ε/k (K) = 481.73

k_1 A_f via A_r and Microscopic Reversbility (MR), $A_r = 1.51 \times 10^{11}$, 86 TSA/HAM for CO + C_2H_3. $E_{a,f} = E_{a,r}$ (4.809) + ΔU_{rxn} (31.52) kcal mol^{-1}.

APPENDIX III

TS INFORMATION AND QRRK ANALYSIS IN CH_2OOH ELIMINATION REACTION SYSTEM

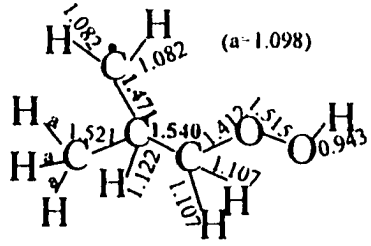
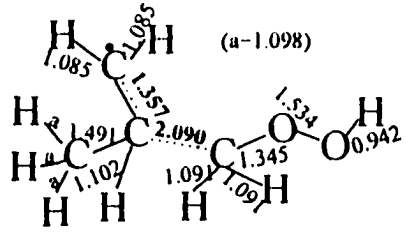
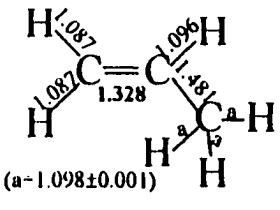
TS III. 1 TS Infromation for C.CCOOH → C_2H_4 + CH_2OOH

	Reactant	Transition State	Product 1 (Alkene)
Bond Lengths (Å)			
Species ID	C.CCOOH	TCJ*CXCQ	C_2H_4
Principal Moments Of Inertia	in unit of cm^{-1}: A = 0.755548 B = 0.072565 C = 0.068077 in unit of 10^{-40}-gram-cm^2: A = 37.049450 B = 385.762064 C = 411.192869	in unit of cm^{-1}: A = 0.279402 B = 0.098401 C = 0.082060 in unit of 10^{-40}-gram-cm^2: A = 100.187777 B = 284.475509 C = 341.123046	in unit of cm^{-1}: A = 5.050953 B = 1.001305 C = 0.835646 in unit of 10^{-40}-gram-cm^2: A = 5.542050 B = 27.956154 C = 33.498204
Symmetry	1	1	4
Internal Rotor(s) And Barrier(s) V (kcal-mol^{-1})	CH_2-CCOOH (1): 0.16 C.C-COOH (1): 3.26 C.CC-OOH (1): 5.40 C.CCO-OH (1): 6.38	CH_2-CCOOH (1): 5.80 C.C-COOH (1): 0.20 C.CC-OOH (1): 5.40 C.CCO-OH (1): 6.38	NO ROTOR
Frequencies (cm^{-1})	39 78 120 165 219 425 461 632 754 800 909 951 1057 1097 1134 1152 1160 1275 1329 1362 1384 1451 1494 2923	-915 39 92 149 209 280 394 437 651 745 821 915 934 955 1026 1074 1096 1189 1288 1321 1348 1451 1658 3040	822 881 984 1054 1093 1307 1328 1829 3128. 3138 3146 3157

TS III. 1 TS Information for C.CCOOH → C_2H_4 + CH_2OOH (Cont')

	2937 2991 3014 3147 3183 3990	3107 3112 3114 3150 3153 3988	

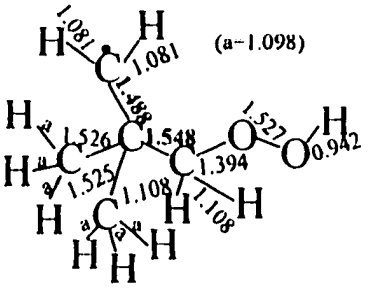
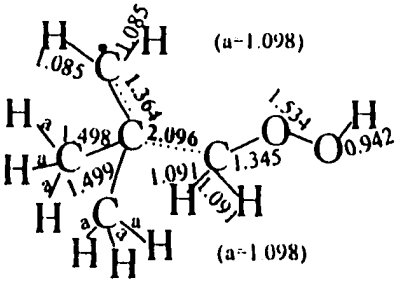
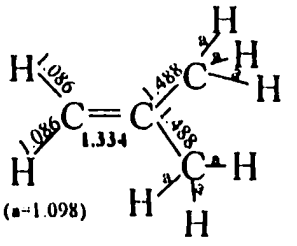
TS III. 2 TS Information for C2.CCOOH → CC=C + CH_2OOH

	Reactant	Transition State	Product 1 (Alkene)
Bond Lengths (Å)			
Species ID	C2.CCOOH	TC2J*CXCQ	CC=C
Principal Moments Of Inertia	in unit of cm^{-1}: A = 0.250388 B = 0.061569 C = 0.053235 in unit of 10^{-40}-gram-cm^2: A = 111.797064 B = 454.654301 C = 525.829879	in unit of cm^{-1}: A = 0.176505 B = 0.071129 C = 0.062813 in unit of 10^{-40}-gram-cm^2: A = 158.594369 B = 393.546252 C = 445.651061	in unit of cm^{-1}: A = 1.518362 B = 0.319380 C = 0.277607 in unit of 10^{-40}-gram-cm^2: A = 18.436071 B = 87.646884 C = 100.835643
Symmetry	3	3	6
Internal Rotor(s) And Barrier(s) V (kcal-mol^{-1})	CH_3-C(C.)COOH (1): 3.87 CH_2-C(C)COOH (1): 0.20 C2.C-COOH (1): 4.20 C2.CC-OOH (1): 5.40 C2.CCO-OH (1): 6.38	CH_3-C(C.)COOH (1): 2.87 CH_2-C(C)COOH (1): 6.00 C2.C-COOH (1): 0.20 C2.CC-OOH (1): 5.40 C2.CCO-OH (1): 6.38	CH_3-C_2H_3 (1): 1.26
Frequencies (cm^{-1})	28 74 119 163 167 216 347 403 480 492 643 798 905 927 955 989 1012 1071 1103	-945 38 95 129 131 202 215 331 429 461 531 664 750 901 923 936 968 997 1034 1079	-113 430 585 895 925 987 1009 1057 1156 1220 1324 1388 1400 1422 1860 3046

TS III. 2 TS Information for C2.CCOOH → CC=C + CH_2OOH (Cont')

	1130 1156 1273 1305 1339 1376 1400 1407 1409 1441 1493 2833 2930 2986 3082 3087 3143 3182 3183 3989	1158 1192 1210 1322 1348 1395 1400 1414 1450 1684 3004 3038 3072 3080 3105 3147 3156 3174 3989	3068 3080 3139 3148 3174

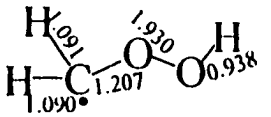
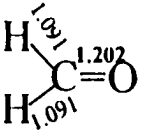
TS III. 3 TS Information for C3.CCOOH → C2C=C + CH_2OOH

	Reactant	Transition State	Product 1 (Alkene)
Bond Lengths (Å)			
Species ID	C3.CCOOH	TC3J*CXCQ	C2C=C
Principal Moments Of Inertia	in unit of cm^{-1}: A = 0.134413 B = 0.057918 C = 0.055484 in unit of 10^{-40}-gram-cm^2: A = 208.258377 B = 483.312996 C = 504.519395	in unit of cm^{-1}: A = 0.134601 B = 0.050499 C = 0.049792 in unit of 10^{-40}-gram-cm^2: A = 207.967001 B = 554.324829 C = 562.190911	in unit of cm^{-1}: A = 0.312646 B = 0.278927 C = 0.156031 in unit of 10^{-40}-gram-cm^2: A = 89.534710 B = 100.358468 C = 179.404128
Symmetry	9	9	18
Internal Rotor(s) And Barrier(s) V (kcal-mol^{-1})	CH_3-C(C2.)COOH (2): 4.70 CH_2-C(C2)COOH (1): 0.20 C3.C-COOH (1): 4.20 C3.CC-OOH (1): 5.40 C3.CCO-OH (1): 6.38	CH_3-C(C2.)COOH (2): 3.87 CH_2-C(C2)COOH (1): 6.20 C3.C-COOH (1): 0.20 C3.CC-OOH (1): 5.40 C3.CCO-OH (1): 6.38	CH_3-C_2H_3(C) (2): 1.26
	13 48 115 157 183 201 264 307 339 410 435 461 569 626 733	-947 36 96 128 136 155 189 207 255 406 416 439 451 549	-116 108 393 423 471 618 932 937 943 985 993 1024 1069

TS III. 3 TS Information for C3.CCOOH → C2C=C + CH_2OOH (Cont')

Frequencies (cm^{-1})	863 922 937 962 976 993 1008 1135 1143 1259 1284 1304 1327 1346 1391 1398 1402 1405 1410 1412 1426 1460 2946 3014 3082 3083 3085 3086.13858 3142 3178 3179 3184 3991	670 752 903 925 935 952 965 984 1032 1057 1079 1190 1317 1327 1343 1388 1395 1400 1404 1415 1445 1446 1690 3033 3070 3071 3078 3080 3098 3145 3157 3171 3172 3989	1312 1323 1382 1390 1397 1398 1399 1477 1873 3073 3074 3074 3077 3147 3148 3173 3175

TS III. 4 TS Information For $CH_2OOH \rightarrow CH_2O + OH$

	Reactant	Product 1 (Formaldehyde)	Product 2 (OH Radical)
Bond Lengths (Å)			
Species ID	CH_2OOH	CH_2O	OH
Principal Moments Of Inertia	in unit of cm^{-1}: A = 1.952583 B = 0.269966 C = 0.237180 in unit of 10^{-40}-gram-cm^2: A = 14.336207 B = 103.689311 C = 118.022837	in unit of cm^{-1}: A = 9.720866 B = 1.305991 C = 1.151313 in unit of 10^{-40}-gram-cm^2: A = 2.879645 B = 21.434012 C = 24.313656	in unit of cm^{-1}: A = 0.000000 B = 20.236922 C = 20.236922 in unit of 10^{-40}-gram-cm^2: A = 0.000000 B = 1.383246 C = 1.383246
Symmetry	1	2	1
Internal Rotor(s) And Barrier(s) V ($kcal\text{-}mol^{-1}$)	CH_2-OOH (1): 6.46 CH_2O-OH (1): 5.98	NO ROTOR	NO ROTOR
Frequencies (cm^{-1})	162 195 197 546 647 1091 1102 1282 1961 3001 3038 3988	1070 1098 1289 1987 2999 3026	3989.03618

TS III. 5 Summary of the Important Bond Lengths

Bond	In reactant	In transition state	In product	Comment
RC.--CCOOH	1.462Å for C.CCOOH	1.347Å for C.CCOOH	1.322Å for C=C	The forming double bond
	1.471Å for C2.CCOOH	1.357Å for C2.CCOOH	1.328Å for CC=C	
	1.488Å for C3.CCOOH	1.364Å for C3.CCOOH	1.334Å for C2C=C	
RC.C--COOH	1.530Å for C.CCOOH	2.096Å for C.CCOOH		The breaking bond
	1.540Å for C2.CCOOH	2.090Å for C2.CCOOH		
	1.548Å for C3.CCOOH	2.096Å for C3.CCOOH		
RC.CC--OOH	1.411Å for C.CCOOH	1.344Å for C.CCOOH		The forming double bond
	1.412Å for C2.CCOOH	1.345Å for C2.CCOOH	1.207Å for C.H_2OOH	in the second step
	1.394Å for C3.CCOOH	1.345Å for C3.CCOOH		
RC.CCO--OH	1.514Å for C.CCOOH	1.535Å for C.CCOOH		The breaking bond in the
	1.515Å for C2.CCOOH	1.534Å for C2.CCOOH	1.930Å for C.H_2OOH	second step
	1.527Å for C3.CCOOH	1.534Å for C3.CCOOH		

TS III. 6 Thermodynamic Properties from MOPAC Calculation

SPECIES	H_{f298}[a]	S_{298}[b]	C_p[b]							DATE	E	L	E	M	E	N	T	
			300	400	500	600	800	1000	1500									
C3.CCOOH	-12.49	101.47	36.53	45.66	53.42	59.59	68.46	74.56	83.88	3/31/97 RU	C	5 H		11 O		2	0 G	6
TC3J*CXCQ[c]	9.54	102.25	36.22	45.04	52.43	58.33	66.92	72.90	82.08	3/31/97 RU	C	5 H		11 O		2	0 G	6
C2.CCOOH	-4.69	96.65	30.82	38.23	44.53	49.55	56.81	61.83	69.47	3/31/97 RU	C	4 H		9 O		2	0 G	5
TC2J*CXCQ[d]	16.29	96.74	30.47	37.58	43.57	48.37	55.37	60.25	67.69	3/31/97 RU	C	4 H		9 O		2	0 G	5
C.CCOOH	2.48	90.39	25.35	31.00	35.81	39.67	45.28	49.17	55.07	3/31/97 RU	C	3 H		7 O		2	0 G	4
TCJ*CXCQ[e]	23.07	90.06	25.03	30.7	35.43	39.17	44.49	48.10	53.56	3/31/97 RU	C	3 H		7 O		2	0 G	4
C2C=C	-3.80	71.00	20.31	25.37	30.13	34.25	40.88	45.91	53.96	3/31/97 RU	C	4 H		8		0	0 G	2
CC=C	4.65	64.20	15.1	18.89	22.43	25.49	30.39	34.11	40.07	3/31/97 RU	C	3 H		6		0	0 G	1
C_2H_4	12.52	52.37	10.44	12.86	15.09	16.98	20.01	22.35	26.15	3/31/97 RU	C	2 H		4		0	0 G	0
CH_2OOH	-14.60	70.56	16.46	18.54	20.26	21.63	23.59	24.90	26.85	3/31/97 RU	C	1 H		3 O		2	0 G	2
CH_2O	-26.00	52.25	8.72	9.74	10.79	11.77	13.44	14.76	16.89	3/31/97 RU	C	1 H		2 O		1	0 G	0
OH	9.50	44.60	6.96	6.96	6.96	6.97	7.03	7.17	7.62	3/31/97 RU	H	1 O		1		0	0 G	0

a Unit in kcal-mol^{-1}.
b Unit in cal-mol^{-1}.
c Transition state for reaction C3.CCOOH -> C2C=C + CH_2OOH
d Transition state for reaction C2.CCOOH -> CC=C + CH_2OOH
e Transition state for reaction C.CCOOH -> C=C + CH_2OOH

TS III. 7 Thermodynamic Analysis for C.CCOOH → C=C + CH_2OOH

	Rx C.CCOOH = TCJ*CXCQ			Rx C.CCOOH = C2H4 + CH2OOH				
	Hf {Kcal/mol} 2.480 23.070			Hf {Kcal/mol} 2.480 12.520 14.600				
	S {cal/mol K} 90.390 90.060			S {cal/mol K} 90.390 52.370 70.560				
	dU (dE) {kcal/mol} (298K) = 20.59			dHr {kcal/mol} (298K) = 24.64 dHr avg (298., 1500. K) = 23.81				
	dUr avg (298., 1500. K) = 20.06			dU (dE) {kcal/mol} (") = 24.05 dUr avg (298., 1500. K) = 22.03				
	for A(T) = Aprime * T^n			Af/Ar (") = 1.947E+02 Af/Ar avg (298., 1500. K) = 4.417E+01				
	Aprime = 6.1334E+11 n = .57148			Fit Af/Ar: A = 2.369E+04 n = -.77 alpha = 9.928E-04 avg error 6.94 %				
Temp(K)	AF(T)	AF-fit(T)	dS(cal/mol K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300	1.44E+13	1.60E+13	8.45E-16	2.46E+01	2.41E+01	3.26E+01	1.94E+02	1.49E+01
400	1.84E+13	1.88E+13	4.73E-12	2.47E+01	2.39E+01	3.28E+01	1.67E+02	1.16E+01
500	2.19E+13	2.14E+13	8.31E-10	2.47E+01	2.37E+01	3.28E+01	1.32E+02	8.33E+00
600	2.50E+13	2.37E+13	2.59E-08	2.47E+01	2.35E+01	3.27E+01	1.03E+02	5.05E+00
800	3.01E+13	2.80E+13	1.86E-06	2.44E+01	2.28E+01	3.23E+01	6.29E+01	-1.44E+00
1000	3.41E+13	3.18E+13	2.38E-05	2.40E+01	2.20E+01	3.19E+01	4.09E+01	-7.85E+00
1200	3.72E+13	3.53E+13	1.28E-04	2.36E+01	2.12E+01	3.15E+01	2.85E+01	-1.42E+01
1500	4.00E+13	4.01E+13	6.71E-04	2.30E+01	2.00E+01	3.10E+01	1.81E+01	-2.36E+01
2000	4.10E+13	4.72E+13	3.34E-03	2.20E+01	1.80E+01	3.04E+01	1.01E+01	-3.89E+01

TS III. 8 Thermodynamic Analysis for C2.CCOOH → CC=C + CH_2OOH

	Rx	C2.CCOOH	= TC2J*CXCQ	Rx	C2.CCOOH	= CC*C	+ CH2OOH
	Hf {Kcal/mol}	-4.690	16.290	Hf {Kcal/mol	- 4.690	4.650	14.600
	S {cal/mol K}	96.650	96.740	S {cal/mol K}	96.650	64.200	70.560
	dU (dE) {kcal/mol} (298K) =		20.98	dHr {kcal/mol} (298K) = 23.94 dHr avg (298., 1500. K) = 22.55			
	dUr avg (298., 1500. K) =		20.62	dU (dE) {kcal/mol} (") = 23.35 dUr avg (298., 1500. K) = 20.77			
	for A(T) = Aprime * T^n			Af/Ar (") = 3.212E+03 Af/Ar avg (298., 1500. K) = 4.790E+02			
	Aprime = 3.4940E+11	n =	.68817	Fit Af/Ar : A = 3.480E+07 n = -1.57 alpha = 6.394E-04 avg error 8.16 %			

Temp(K)	AF(T)	AF-fit(T)	dS(cal/mol K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300	1.78E+13	1.77E+13	5.43E-16	2.39E+01	2.34E+01	3.81E+01	3.20E+03	1.25E+01
400	2.19E+13	2.16E+13	3.56E-12	2.39E+01	2.31E+01	3.81E+01	2.36E+03	8.69E+00
500	2.52E+13	2.52E+13	6.83E-10	2.38E+01	2.28E+01	3.78E+01	1.63E+03	4.90E+00
600	2.83E+13	2.85E+13	2.25E-08	2.36E+01	2.24E+01	3.74E+01	1.12E+03	1.14E+00
800	3.41E+13	3.48E+13	1.73E-06	2.31E+01	2.15E+01	3.66E+01	5.71E+02	-6.26E+00
1000	4.02E+13	4.05E+13	2.30E-05	2.25E+01	2.05E+01	3.60E+01	3.32E+02	-1.35E+01
1200	4.61E+13	4.60E+13	1.29E-04	2.19E+01	1.96E+01	3.55E+01	2.16E+02	-2.07E+01
1500	5.41E+13	5.36E+13	7.09E-04	2.12E+01	1.82E+01	3.49E+01	1.29E+02	-3.12E+01
2000	6.57E+13	6.53E+13	3.83E-03	2.00E+01	1.60E+01	3.42E+01	6.82E+01	-4.85E+01

TS III. 9 Thermodynamic Analysis for C3.CCOOH → C2C=C + CH_2OOH

Rx	C3.CCOOH	= TC3J*CXCQ	Rx	C3.CCOOH	= C2C*C	+ CH2OOH
Hf {Kcal/mol}	-12.490	9.540	Hf {Kcal/mol}	-12.490	-3.800	14.600
S {cal/mol K}	101.470	102.250	S {cal/mol K}	101.470	71.000	70.560
			dHr {kcal/mol} (298K) = 23.29 dHr avg (298., 1500. K) = 21.34			
dU (dE) {kcal/mol} (298K) = 22.03			dU (dE) {kcal/mol} (") = 22.70 dUr avg (298., 1500. K) = 19.56			
dUr avg (298., 1500. K) = 21.16			Af/Ar (") = 8.701E+03 Af/Ar avg (298., 1500. K) = 8.744E+02			
for A(T) = Aprime * T^n			Fit Af/Ar: A = 4.701E+09 n = -2.26 alpha = 3.985E-04 avg error			
Aprime = 4.6599E+12	n = .31773		10.53 %			

Temp(K)	AF(T)	AF-fit(T)	dS(cal/mol K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300	2.51E+13	2.85E+13	1.32E-16	2.33E+01	2.27E+01	4.01E+01	8.65E+03	1.13E+01
400	3.10E+13	3.13E+13	1.35E-12	2.32E+01	2.24E+01	3.98E+01	5.71E+03	7.26E+00
500	3.53E+13	3.36E+13	3.36E-10	2.30E+01	2.20E+01	3.93E+01	3.49E+03	3.31E+00
600	3.84E+13	3.56E+13	1.31E-08	2.26E+01	2.14E+01	3.87E+01	2.14E+03	-5.95E-01
800	4.21E+13	3.90E+13	1.23E-06	2.18E+01	2.03E+01	3.76E+01	9.13E+02	-8.22E+00
1000	4.39E+13	4.18E+13	1.81E-05	2.11E+01	1.91E+01	3.67E+01	4.71E+02	-1.56E+01
1200	4.48E+13	4.43E+13	1.06E-04	2.04E+01	1.80E+01	3.61E+01	2.84E+02	-2.29E+01
1500	4.57E+13	4.76E+13	5.94E-04	1.94E+01	1.64E+01	3.54E+01	1.59E+02	-3.36E+01
2000	4.81E+13	5.22E+13	3.16E-03	1.80E+01	1.40E+01	3.45E+01	7.92E+01	-5.11E+01

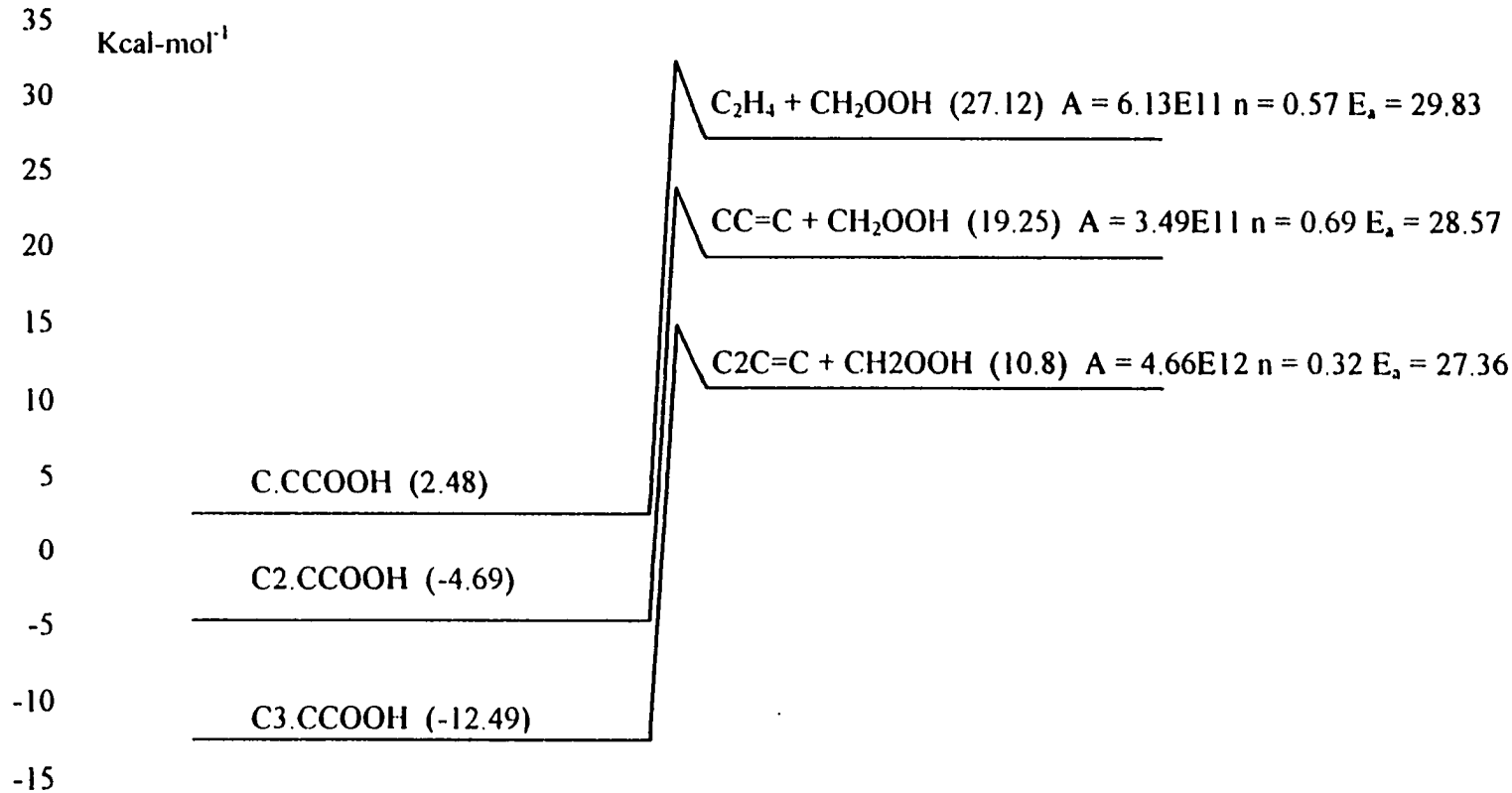
TS III. 10 Thermodynamic Analysis for $CH_2OOH \rightarrow CH_2O + OH$

Rx	CH2OOH =	CH2O +	OH
Hf {Kcal/mol}	14.600	-26.000	9.500
S {cal/mol K}	70.560	52.250	44.600

dHr {kcal/mol} (298K) = -31.10
dHr avg (298., 1500. K) = -32.68
dU (dE) {kcal/mol} (") = -31.69
dUr avg (298., 1500. K) = -34.47
Af/Ar (") = 8.382E+00
Af/Ar avg (298., 1500. K) = 1.024E+00
Fit Af/Ar: A = 2.191E+06 n = -2.16 alpha = 1.667E-04

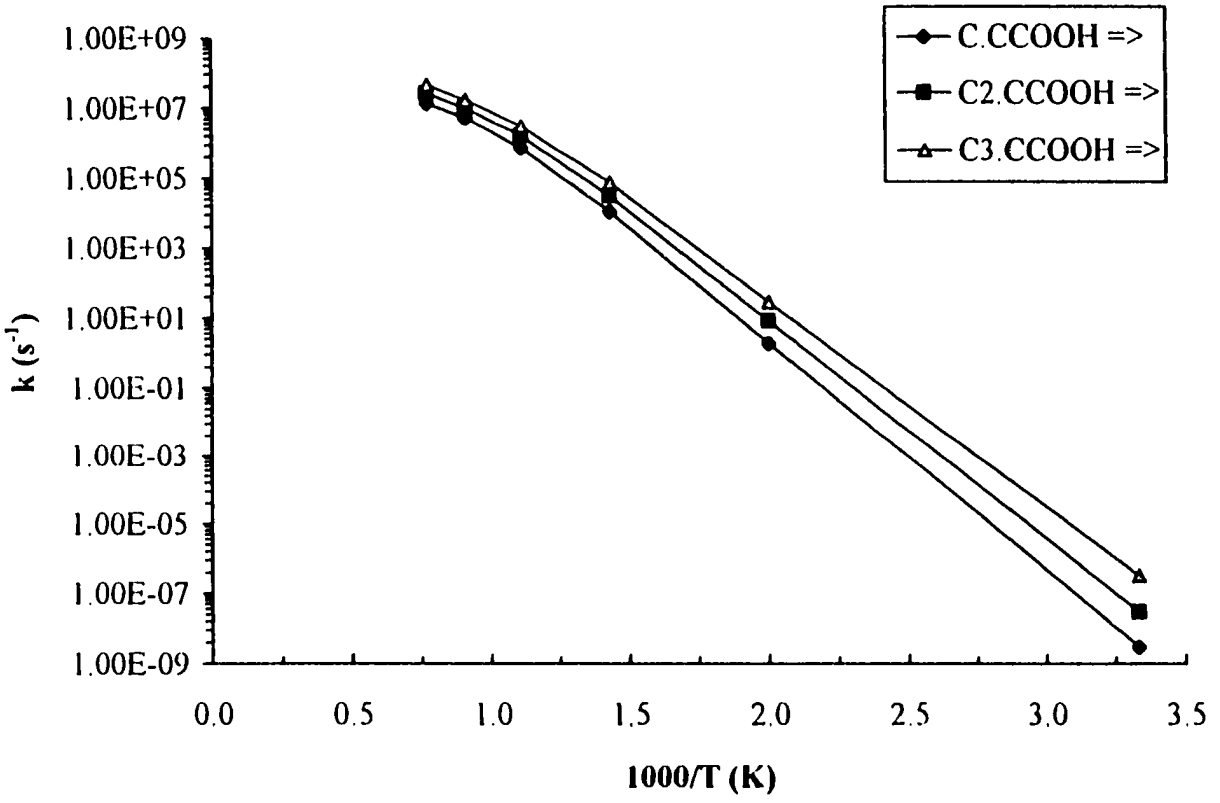
Temp(K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	(Af/Ar)	dG(Kcal/mol)
300	-3.11E+01	-3.17E+01	2.63E+01	8.31E+00	-3.90E+01
400	-3.12E+01	-3.20E+01	2.59E+01	5.24E+00	-4.16E+01
500	-3.14E+01	-3.24E+01	2.55E+01	3.30E+00	-4.42E+01
600	-3.17E+01	-3.29E+01	2.50E+01	2.15E+00	-4.67E+01
800	-3.23E+01	-3.39E+01	2.41E+01	1.04E+00	-5.16E+01
1000	-3.29E+01	-3.49E+01	2.34E+01	5.86E-01	-5.63E+01
1200	-3.35E+01	-3.59E+01	2.29E+01	3.76E-01	-6.10E+01
1500	-3.43E+01	-3.72E+01	2.23E+01	2.26E-01	-6.78E+01
2000	-3.53E+01	-3.93E+01	2.17E+01	1.26E-01	-7.88E+01

TS III. 11 Potential Energy Diagrams for (R1R2C)CCOOH → R1R2C=C + CH_2OOH

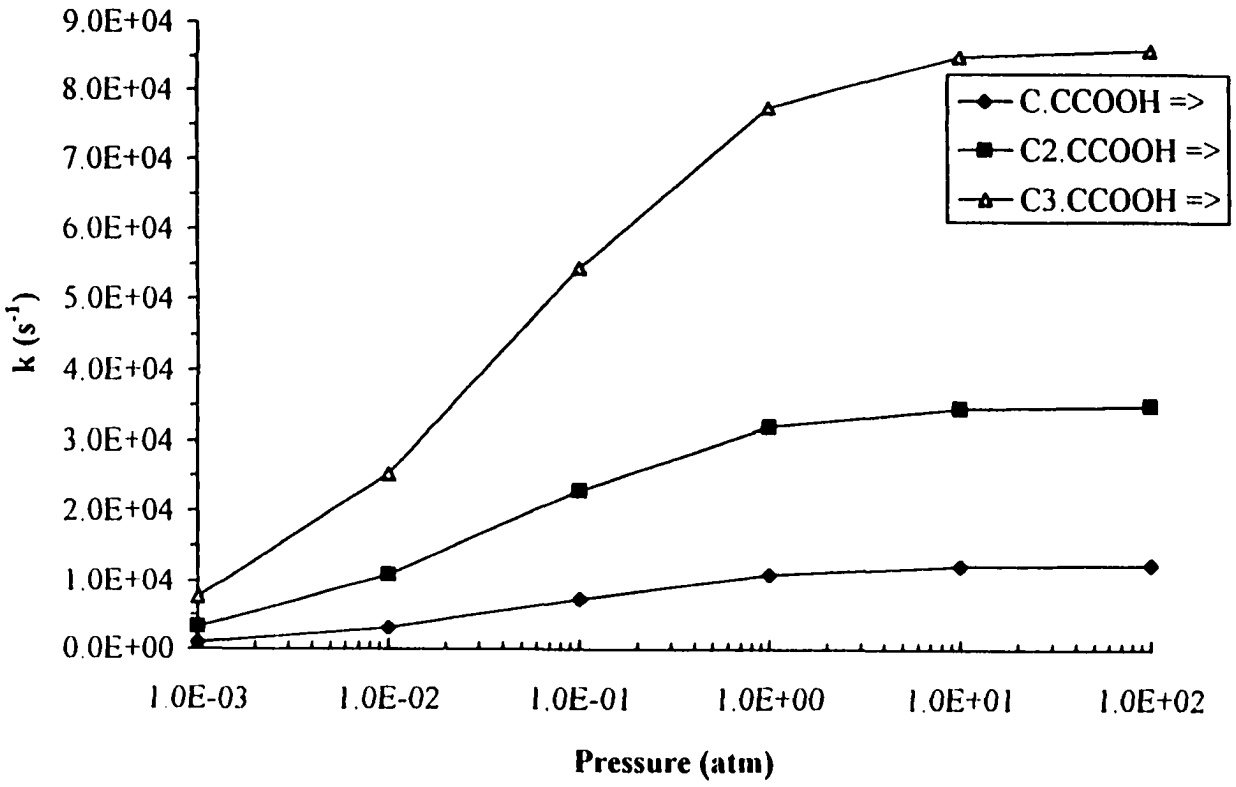


A are from thermodynamic analysis as in TS III. 6 - III. 8
E_a are from ($E_{a,r}$ (7.8) + ΔU) Kcal-mol^{-1}

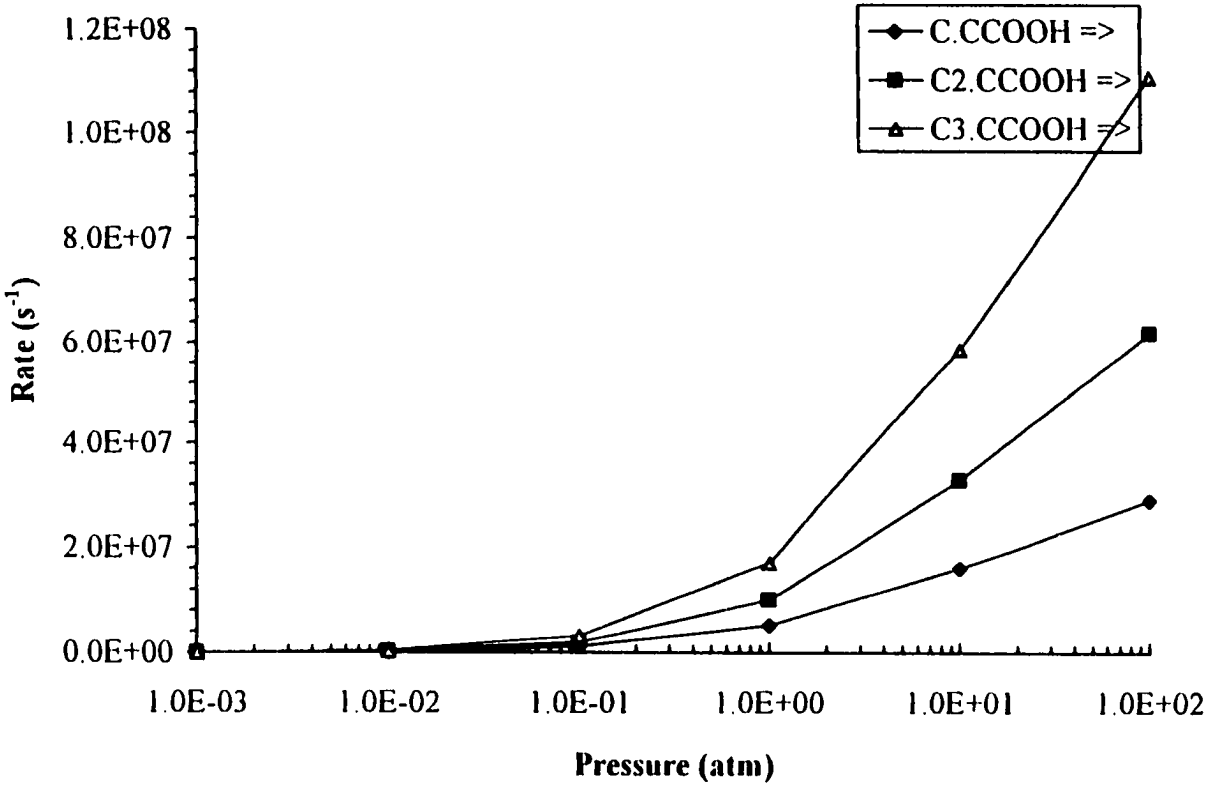
TS III. 12 Temperature Dependence of Rate Constants at 1 Atm



TS III. 13 Pressure Dependence of Rate Constants at 700 K



TS III. 14 Pressure Dependence of Rate Constants at 1100 K



TS III. 15 Activation Energy Analysis

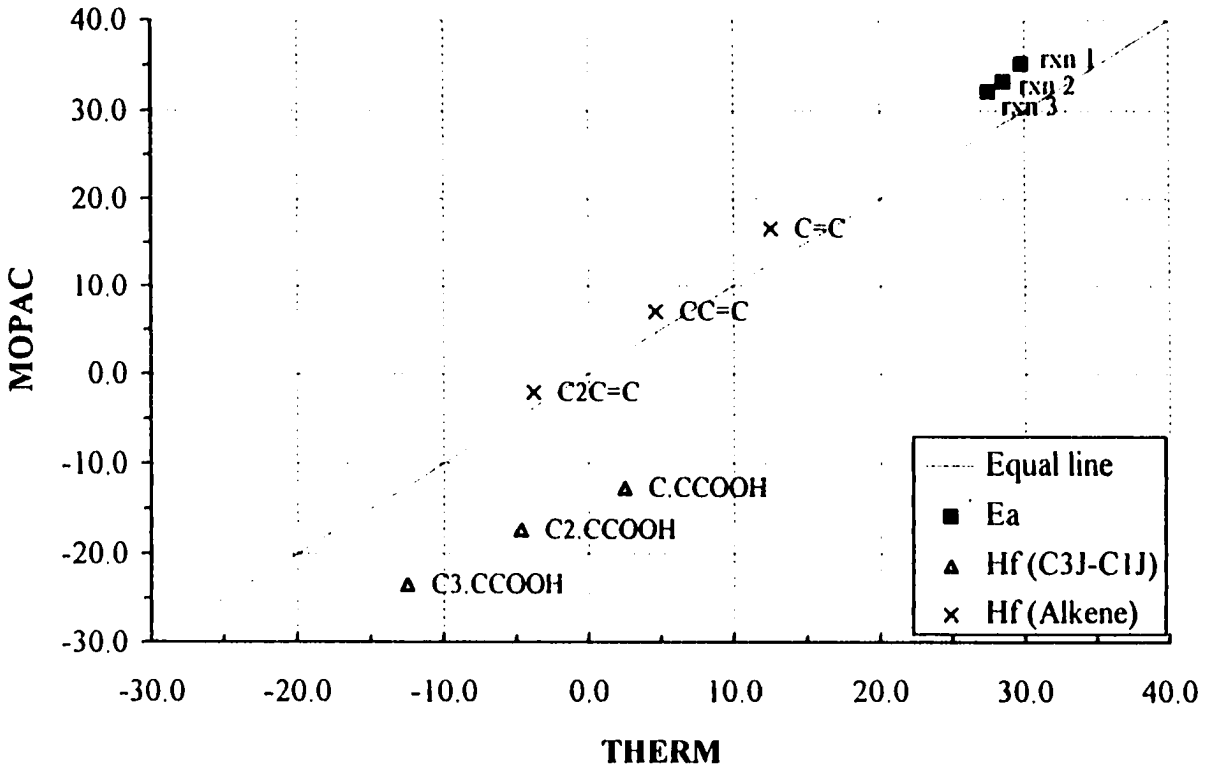


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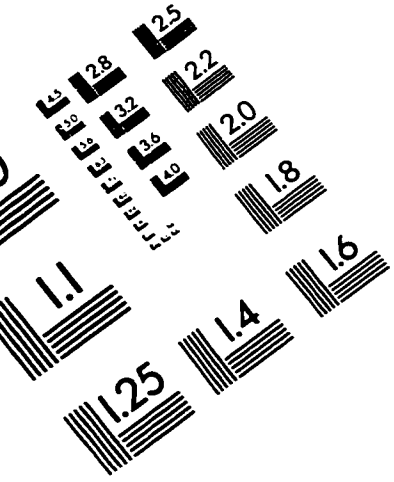
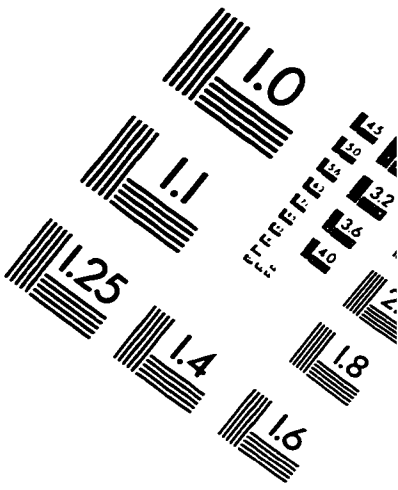
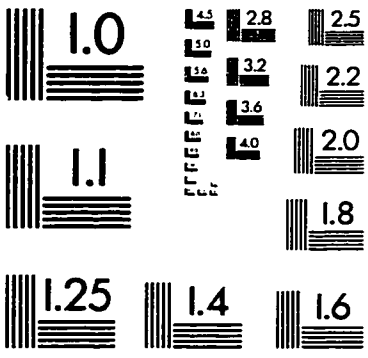
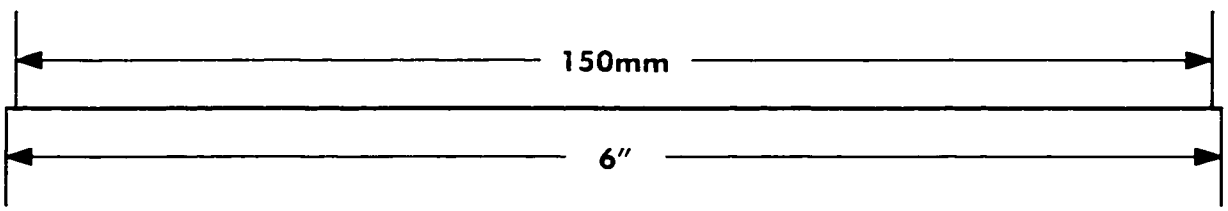
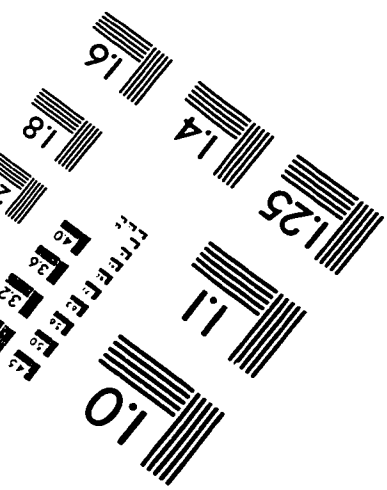
IMAGE EVALUATION TEST TARGET (QA-3)

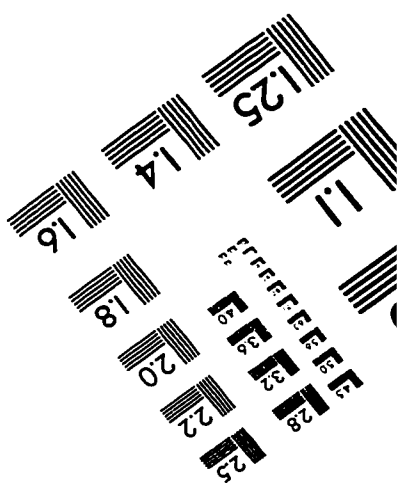












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